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EXPERIMENTS
IN
GENERAL CHEMISTRY
AND
INTRODUCTION TO
CHEMICAL ANALYSIS

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INTRODUCTORY NOTE.

This little book is a translation of the papyrograph notes, the principal part of which was prepared by Professor Volhard while in charge of the work in inorganic chemistry in the laboratory of the University of Munich. The notes were afterwards continued and completed by Professor Zimmermann, as nearly as possible in the spirit of the first part.

I have been familiar with the original notes for some time, and have felt that their use in American laboratories would be in the interest of thorough instruction in general chemistry. A few years ago Dr. Edward Renouf, who had been connected with the laboratory of Munich for a number of years, and who had been a student and assistant of Professor Volhard, was engaged as assistant in the laboratory of the Johns Hopkins University. As he was thoroughly familiar with the Volhard system, this offered a good opportunity to introduce it. Accordingly, Dr. Renouf undertook the translation of the book, and it was issued in the form of papyrograph sheets. In this form it has been in use in the laboratory of the Johns Hopkins University for some time. As we have convinced ourselves of the value of the system by observation of its working in the laboratory, it has seemed desirable to put the book in type.

In this laboratory it is used as an introduction to analytical work by those who are intending to devote themselves to Chemistry as a specialty. For a few years it was used by undergraduate students in their second year, but experience has led us to the conclusion that the course is too technical for profitable use by any except those who have chosen Chemistry as their life-work.

IRA REMSEN.

EXPERIMENTS IN GENERAL CHEMISTRY

AND

INTRODUCTION TO CHEMICAL ANALYSIS.

1. POTASSIUM CHLORIDE.

Heated in a test tube the salt decrepitates (?), then fuses. The fused mass is found, after cooling, to be crystalline.

Hold a fragment of the fused salt on a platinum wire in the blue flame of the Bunsen burner; it colors the flame violet. This is a general reaction of potassium salts. Look at the flame through a piece of cobalt glass; it appears reddish (?).

The salt is easily soluble in water. Test the reaction of the aqueous solution with litmus paper (?). How does the salt taste? Evaporate a few drops of the solution by heating gently on a watch-glass. Crystals of the salt separate from the solution. Examine them with the microscope.

Perchloric acid added to the solution causes a crystalline precipitate (?). This is soluble in boiling water, insoluble in alcohol.

Add a solution of *tartaric acid* to the solution of potassium chloride; at first the solution remains clear. After standing a few moments, a crystalline precipitate is formed. The precipitation is hastened by shaking the flask or stirring with a glass rod. This precipitate is monopotassium tartrate. Collect about a teaspoonful, filter, and wash with alcohol. After washing the precipitate, test its reaction with litmus paper; try its solubility in water; it dissolves in boiling water. Put about 2 cc. of the tartrate in a test tube; add solution of sodium carbonate cautiously; the salt dissolves and a gas escapes (?). Add just enough sodium carbonate to dissolve the tartrate; what does the solution contain? Now add to this solution, drop by drop, a little hydrochloric acid; the precipitate of monopotassium tartrate again appears. Why? More hydrochloric acid dissolves it (?). From this solution in hydrochloric acid it is again precipitated by sodium carbonate (?). Dry the rest of the tartrate and fuse in a porcelain dish or crucible; boil the fused mass with water, and filter. A residue of charcoal remains on the filter; a few drops evaporated on platinum foil leave a white residue (?). The filtrate has an alkaline reaction, and forms with calcium or barium salt solutions, white precipitates. Acids evolve from it a gas (?) which, conducted into a solution of barium or calcium hydroxide, forms a white precipitate soluble in acids (?).

Add to a drop of the solution of potassium chloride, in a test tube, a few drops of *platinum chloride*; a finely divided yellow precipitate is formed, easily soluble in hot water, insoluble in alcohol (?). Dissolve by adding

a little water and boiling; pour the hot solution on a watch-glass; on cooling it crystallizes; examine the crystals with the microscope (?).

By adding *aluminium sulphate* to the solutions of potassium salts a precipitate of alum is formed (?). On heating the solution it dissolves; on cooling it recrystallizes. What is the crystalline form of alum (?). What is the composition of the crystals?

Treated with concentrated *sulphuric acid*, potassium chloride foams, and a colorless gas escapes (?), of penetrating odor, forming a heavy vapor when it comes in contact with the air (?). It imparts a red color to blue litmus paper. Hold a drop of silver nitrate on a stirring-rod over the mouth of the tube; it becomes white (?).

Pour concentrated sulphuric acid on a teaspoonful of potassium chloride in a small flask; fit a cork to the flask; bore the cork to fit a tube bent twice at right angles; conduct the gas through the tube into a test tube which contains a little water. The end of the conducting tube must not reach the surface of the water (?). Heat the flask moderately to hasten the evolution of the gas; water absorbs it largely; this solution, hydrochloric acid, is heavier than water; notice how it sinks as it forms in the water in the tube; it has a strong acid taste and reaction: added to carbonates, carbon dioxide escapes (?).

Hydrochloric acid dissolves many metals—for example, iron and zinc—its hydrogen escaping as gas (?). In these reactions the salts of the hydrochloric acid *chlorides*, are formed. These are mostly soluble in water; silver chloride and mercurous chloride are insoluble; lead chloride is soluble with difficulty; hence soluble chlorides and hydrochloric acid form precipitates with solutions of silver, lead, or mercurous salts.

Silver chloride is white, curdy, clots together when the tube is shaken, insoluble in water and dilute nitric acid, soluble in ammonia, potassium cyanide, and sodium hyposulphite. When only minute traces of hydrochloric acid or chlorides are present, a whitish cloud is formed in the silver solution.

Mercurous chloride is white, insoluble in dilute acids, soluble in chlorine water (?), or concentrated nitric acid (?). Ammonia turns it black.

Lead chloride is white, soluble in much boiling water, crystallizing when the solution cools.

Mix in a mortar equal quantities of potassium chloride and manganese dioxide; bring a little of the mixture into a test tube, pour a teaspoonful of concentrated sulphuric acid slowly into a teaspoonful of water in another tube, then add this diluted acid to the mixture in the first tube. Warm gently *under the hood.* A gas escapes; this is not the colorless hydrochloric acid; it is greenish yellow, chlorine (?). Chlorine has a suffocating odor, bleaches moist litmus paper (?), turns brown a strip of paper moistened with potassium iodide (?). Chlorine is soluble in water, though much less so than hydrochloric acid. The solution has the color and odor of the gas, bleaches organic colors (litmus, indigo); changes the lower oxides into higher ones (sulphurous acid, arsenious

oxide, ferrous chloride), and dissolves many metals (gold).

2. POTASSIUM NITRATE (SALTPETRE).

It melts easily when heated in a tube; the cooled mass is crystalline. If the melted salt is heated higher, a colorless and inodorous gas is evolved. Test the nature of the gas by holding an ignited match in the opening of the tube (?). [Preserve the residue.]

On the platinum wire it imparts a violet color to the flame (?).

Heat a little saltpetre on charcoal with the blowpipe; a rapid combustion is observed, and an evolution of gas which causes the fused mass to sputter. Why the combustion, and whence the gas? What has become of the saltpetre? What is the residue upon the charcoal? To collect some of the residue for examination, put a little powdered saltpetre on the charcoal and touch it with an ignited match; combustion begins at once. By adding successively small quantities of saltpetre to the sputtering mass the combustion can be kept up, and is soon less intense, so that it is easy to collect enough of the residue for examination; at last hold the charcoal a few moments in the blue gas flame and heat the residue sharply. Scrape the residue from the charcoal, dissolve in a little water, and filter. Test the filtrate with litmus paper, with hydrochloric acid, and with barium chloride (?).

Fuse saltpetre in a test tube and drop small pieces of sulphur on the melted saltpetre; the sulphur burns with an intense light and forms a salt of sulphuric acid (?).

Mix saltpetre with powdered potassium ferrocyanide and heat a *small* piece (size of a pea) on the platinum foil; it explodes when heated (?).

Saltpetre is much more easily soluble in hot than in cold water. Prepare a saturated solution (?) in hot water and let it cool undisturbed. Form of the crystals (?), reaction of the solution (?). Behavior with those reagents which give characteristic reactions with potassium salts (?).

Pour concentrated sulphuric acid on a little dry saltpetre; no gas bubbles are observed, but on warming the tube a colorless or yellowish vapor is evolved, of penetrating odor; the vapor reddens blue litmus paper; it forms no precipitate in a drop of silver nitrate on a stirring-rod; hold a drop of ammonia on a stirring-rod over the mouth of the tube and a heavy white vapor is formed (?). Weigh 20 grams of saltpetre and bring it into a small retort with glass stopper; weigh and add 20 grams concentrated sulphuric acid; place a small flask over the neck of the retort and warm the retort; the vapor collects and is condensed in the flask, forming a yellowish liquid which boils at 86°, and if heated a short time becomes colorless. This liquid is anhydrous nitric acid. Test its behavior with metals (copper, mercury, tin) and with organic substances (starch or sugar). Dilute the remainder with four times its volume of water, and repeat these tests with the dilute acid. Write equations for the reactions with the metals.

Add to an aqueous solution of saltpetre and potassium chloride, concentrated sulphuric acid, and warm the mixture; chlorine is evolved (?). Test for chlorine (?).

Color an aqueous solution of saltpetre with a few drops of indigo solution; add concentrated sulphuric acid and heat gently; the color of the indigo disappears (?). An addition of potassium chloride causes the color to disappear more quickly (?). An aqueous solution of saltpetre when mixed with potassium chloride does not evolve chlorine, nor does it destroy the color of the indigo solution unless sulphuric acid be added; substitute nitric acid for the saltpetre solution and the reactions occur *without* addition of sulphuric acid. What is the difference between nitric acid and nitrates in their behavior toward oxidizable substances?

Mix an aqueous solution of saltpetre with concentrated sulphuric acid, add a piece of copper foil and heat gently; a gas, at first red, then colorless, is evolved; conduct the gas into a solution of ferrous sulphate, the solution is colored dark brown (?). Repeat this experiment, using a crystal of ferrous sulphate instead of the copper foil (?).

Add to *one* drop of aqueous solution of saltpetre two or three cc. concentrated sulphuric acid; this liquid should be warm, but not hot; prepare a cold aqueous solution of ferrous sulphate; pour this very carefully into the tube containing the saltpetre and sulphuric acid; if due care in pouring is taken, the ferrous sulphate solution will remain above the heavier sulphuric acid; a brown ring is seen at the point of contact of the two liquids; if only a trace of saltpetre be present the ring is amethyst colored. This is a very delicate test for nitric acid.

Boil an aqueous solution of saltpetre with zinc dust for ten minutes and filter. Add to a part of the filtrate a drop of potassium permanganate solution and some dilute sulphuric acid; the color disappears (?). To another part of the filtrate add potassium iodide, dilute starch paste and dilute sulphuric acid; a blue color appears (?). An aqueous solution of saltpetre treated in the same way is not colored blue.

An aqueous solution of the residue obtained by heating saltpetre in a glass tube behaves in the same way as the solution obtained by boiling saltpetre with zinc dust and water.

Add to an aqueous solution of saltpetre, sodium hydroxide, zinc dust and iron filings; heat the mixture gently in a flask; ammonia is evolved (?); it can be recognized by the odor and by testing with litmus paper (?).

3. POTASSIUM SULPHATE.

It decrepitates when heated, and is harder to fuse than potassium chloride or saltpetre; it suffers no further change when fused in a tube.

The flame reaction indicates potassium; prove its presence with reagents.

Dissolve the salt in boiling water; allow it to crystallize. What is the form of the crystals (?). What is the composition of the crystallized salt (?). How does it taste (?). What is the reaction of the aqueous solution (?).

Heat a fragment of the decrepitated salt on charcoal or on the platinum wire with the reducing flame (?). It fuses and is reduced (?). Note the peculiar glowing of the hot mass.

The fused substance—potassium sulphide—is reddish yellow in color. When cold, remove it from the coal and place it on a watch-glass; lay a fragment on a silver coin and moisten with water. It has an alkaline reaction (?) and stains the silver black (?). Add a drop of dilute sulphuric acid, and you will detect the odor of sulphuretted hydrogen (?). Dissolve the remainder of the fused sulphide in water, and add a drop of sodium nitro-prussiate; the solution is colored purple. (General reaction for all soluble sulphides.)

What are the principal compounds which show an alkaline reaction (?). The soluble sulphides are those of the alkali metals and of the alkaline earth metals. If it is desired to test for sulphur in compounds of other metals by the reactions mentioned, mix sodium carbonate with the substance before reducing on charcoal. Why is this necessary (?).

Potassium sulphate dissolves in concentrated sulphuric acid when gently heated; no gas is evolved. Excepting the sulphates, all compounds which contain sulphur (*i. e.* the sulphides and the salts of those acids of sulphur which contain less oxygen than sulphuric acid) evolve with concentrated sulphuric acid, sulphur dioxide, recognizable by its odor (?).

Dissolve potassium sulphate in very little hot concentrated sulphuric acid; crystals of another salt separate on cooling (?).

Sulphuric acid is a dibasic acid (?). How is sulphuric acid manufactured? What is the behavior of the concentrated acid with water? with wood? paper? sugar? copper? mercury? How does the dilute acid behave with zinc? iron?

Sulphuric acid is a very strong (?) acid, and a high temperature is necessary to volatilize it. For these reasons it is employed in isolating the volatile acids, as well in manufacture as in testing for them, as has been shown with hydrochloric and nitric acids.

The sulphates are mostly soluble in water; calcium sulphate requires much water for solution; strontium sulphate more, lead sulphate still more, and barium sulphate is practically insoluble. These sulphates are obtained as white precipitates when solutions of sulphuric acid or other sulphates are added to solutions of calcium, strontium, lead, or barium salts. Note the appearance and composition of these precipitates.

In testing for sulphuric acid, in separating it from other substances, and in determining the weight of the amount present in a solution, the acid is usually precipitated as barium sulphate by adding barium chloride to a solution of the substance in hydrochloric acid. Note that hydrochloric and nitric acids, if concentrated, form also white precipitates with barium salts (?). These precipitates present a different appearance from barium sulphate, and dissolve when much water is added. More water is needed to dissolve the precipitates formed in barium chloride by nitric acid than that formed by hydrochloric acid (?).

4. POTASSIUM CHLORATE.

When heated in the tube it fuses readily and then evolves much oxygen (?).

Heated on charcoal it behaves like saltpetre, but the combustion is more violent. Collect the residue after heating on charcoal as described with saltpetre; examine it (?).

Use very small fragments of the chlorate, not larger than a grain of rice, for the two following experiments.

Heated with potassium ferrocyanide the chlorate explodes with sharp report. Mix a little chlorate with sulphur or antimony sulphide, put it in a porcelain mortar and rub with the pestle; it ignites and explodes with sharp detonation.

Potassium chlorate is not easily soluble in cold water; dissolve in hot water and crystallize; reaction (?); taste (?).

All chlorates are soluble in water; hence no chlorates are precipitated when potassium chlorate is added to solutions of metal salts. At high temperatures the chlorates act as oxidizing agents. When fused with potassium chlorate almost all oxidizable substances are changed to their highest oxides (?), but in neutral aqueous solution the salt does not give up its oxygen readily. In aqueous solution free chloric acid is a very powerful oxidizer; therefore the solution of potassium chlorate acts as an oxidizer if dilute sulphuric acid be added. Test with indigo solution (?); with ferrous sulphate (?); with sulphurous acid (?); add dilute hydrochloric acid to a crystal of potassium chlorate and heat gently; a gas escapes (?).

Free chloric acid is stable only in cold aqueous solution; when heated, or when the water is evaporated from its solution, it decomposes. If, then, concentrated sulphuric acid is poured on potassium chlorate, chloric acid is set free, but decomposes at once. Take a fragment of potassium chlorate not larger than a grain of rice, and pour a drop or two of concentrated sulphuric acid upon it; the acid assumes a dark yellow color; when gently warmed, a dark yellow heavy gas, chlorine tetroxide, is evolved (?); heated higher, this gas is decomposed with explosion.

How is potassium chlorate made?

5. POTASSIUM BROMIDE.

In the glass tube and on the platinum wire it behaves like potassium chloride.

In water it is easily soluble; reaction and taste of the solution (?); crystallize by slow evaporation; form of the crystals (?).

Add to one cc. of concentrated sulphuric acid five or six drops of water, and pour the mixture on a fragment of potassium bromide. Hydrobromic acid is set free, which by gentle heat is evolved as a colorless gas with the same properties as hydrochloric acid gas. The aqueous solution of the gas resembles aqueous hydrochloric acid.

Repeat this experiment without diluting the concentrated sulphuric acid. The hydrobromic acid evolved is colored yellow by free bromine (?). The more sulphuric acid is used, the darker the color will be.

Touch starch with a wet stirring-rod and insert it in the mouth of the tube; the bromine colors the starch yellow.

Mix potassium bromide with an equal quantity of manganese dioxide or potassium bichromate; bring the mixture in a flask (same as used in making hydrochloric acid); add dilute sulphuric acid (2 vol: conc. acid, 3 vol. water) and distill into a test tube. Bromine escapes as dark brown vapor which condenses in the tube, forming a liquid of dark reddish brown color and disagreeable odor. (Perform this last experiment under the hood.)

Bromine dissolves in water, forming a red solution which behaves like chlorine water; it bleaches and oxidizes, but is a little weaker than chlorine. Test this by suitable experiments.

Ether, chloroform, or carbon disulphide shaken with the aqueous solution extracts the bromine from it, becoming colored yellow to brown according to the proportion of bromine. Shake these solutions with sodium hydroxide or potassium hydroxide; the ether (or chloroform or carbon disulphide) becomes colorless, showing that the bromine has passed into the sodium hydroxide (?). Acidulate (?) the colorless alkaline solution with dilute sulphuric acid; it becomes yellow, and when heated, vapors of bromine escape (?).

Metals dissolve in bromine water without evolution of a gas (?).

Chlorine water colors solutions of bromides or hydrobromic acid yellow (?). If only traces of bromine compounds are present it may be impossible to see the change of color; but if a little ether, chloroform, or carbon disulphide be added and the mixture shaken, the traces of bromine will be absorbed by the solvent and can then be seen.

Dilute nitric or *nitrous acids* do not evolve bromine from a solution of potassium bromide. Heat with concentrated nitric acid, bromine is evolved (?).

Silver nitrate precipitates from soluble bromides silver bromide (?), yellowish white, soluble with difficulty in ammonia, otherwise resembling silver chloride (?).

Mercurous nitrate precipitates yellowish white mercurous bromide (?), easily soluble in chlorine water; the solution is reddish yellow (?).

Lead acetate precipitates white lead bromide, easily soluble in nitric acid.

6. POTASSIUM IODIDE.

Heated in the tube or on the wire, it behaves like potassium bromide, but is somewhat volatile; heated on charcoal, a white coating forms on the coal (?).

The iodide is easily soluble in water; reaction and taste of solution (?).

When concentrated sulphuric acid acts on potassium iodide there is no evolution of hydriodic acid, but iodine escapes.

In order to recognize the different phases of this reaction more clearly, proceed as follows: Bring a piece of potassium iodide the size of a pea in a dry test tube; add *one* drop of water and three or four drops of concentrated sulphuric acid; the salt becomes

brown; heat gently; violet colored vapor (?) escapes, and with it a gas which you will recognize by smelling it, or holding a strip of paper moistened with lead acetate in the opening of the tube (?); at the same time a yellow coating forms on the inside of the tube above the acid (?). Add five or six drops more of the acid and continue to heat gently; the bad odor first noticed disappears gradually, and another, quite different odor, piercing and irritating to the throat, is now perceptible (?).

Express the above reactions in equations.

Concentrated sulphuric acid does not decompose hydrochloric acid; it decomposes hydrobromic acid partly, and hydriodic fully.

Powder and mix a fragment of iodide the size of a pea with the same quantity of manganese dioxide; put into a dry test tube, add 10 or 12 drops dilute sulphuric acid, and heat gently. Iodine sublimes in the upper half of the tube. What are the properties of iodine (?).

With a stirring-rod take out small fragments of iodine from the tube, and test its behavior with water (?), alcohol (?), ether (?), chloroform (?), carbon disulphide (?), aqueous solution of potassium iodide (?), aqueous solution of sulphurous acid (?), sulphuretted hydrogen water (?), iron filings (?), starch paste (?).

Chlorine sets free the iodine from hydriodic acid or iodides, taking the place of the iodine in the compound. By adding chlorine water continuously, the solution of potassium iodide first becomes brown (?); more chlorine water makes the color darker; then the iodine commences to separate as a solid, at first reddish brown and voluminous, then changing to the form of a dark gray crystalline powder resembling graphite. Continue to add chlorine water; the color of the liquid becomes clearer until all the iodine has separated. Add still more chlorine water; the iodine dissolves (?) and at last a clear colorless solution is obtained (?). From this solution the iodine can be separated by cautiously adding sulphurous acid (?). More sulphurous acid causes the iodine to disappear again (?); and now chlorine water added to the colorless solution separates iodine again. Bromine water acts like chlorine water in this reaction.

Nitric acid, nitrous acid, nitrogen dioxide, and many other oxidizing agents separate iodine from hydriodic acid or acidulated solutions of iodides. From very dilute solutions the iodine does not separate in solid form, but remains in solution. The solution is then more or less brown. If the solution of the iodide is very dilute, as, for example, in mineral waters, no color is seen. The minutest trace of iodine can be detected by first adding a little starch paste to the solution and then liberating the iodine, or by shaking the solution which contains free iodine with chloroform or carbon disulphide. These reagents extract the iodine from the aqueous solution and are colored by it.

If we wish to test for minute traces of iodine, it is better to separate the iodine with nitrous acid, *i. e.* with dilute sulphuric acid to which red fuming nitric acid (?) or potassium nitrite has been added; because an excess of nitrous acid does not act further upon the free iodine, as we have seen chlorine does.

Silver nitrate precipitates from solutions of hydriodic acid or iodides yellowish silver iodide, resembling silver chloride in its properties, except that it is nearly insoluble in ammonia.

Mercurous nitrate precipitates greenish yellow mercurous iodide, soluble in, but at the same time decomposed by potassium iodide.

Mercuric nitrate precipitates bright red mercuric iodide (?), soluble in potassium iodide and in mercuric salts.

Lead acetate precipitates lemon-yellow lead iodide.

Copper sulphate precipitates a mixture of cuprous iodide and iodine (?). Copper sulphate mixed with sulphurous acid precipitates white cuprous iodide (?).

Boil potassium iodide with a ferric salt (iron ammonium sulphate) in a distilling flask. All iodine distills off (?).

Add chlorine water gradually to a solution containing an iodide and a bromide; the iodine separates first, then dissolves; when all the iodine is oxidized, and not till then, a further addition of chlorine water sets the bromine free.

If at the beginning of the experiment a little starch paste is added to the solution of the iodide and bromide, the solution, on adding chlorine, assumes a blue color, which gradually disappears and gives place to the yellow color which is characteristic of the action of bromine on starch. If but little bromine be present, it is better to use carbon disulphide instead of starch. The carbon disulphide becomes at first violet, then brown.

To test for potassium chloride in commercial potassium iodide, add to the aqueous solution silver nitrate as long as this causes precipitation; shake the mixture with an equal volume of ammonia, and filter. If chlorine be present, the filtrate forms a white precipitate of silver chloride when acidulated with nitric acid.

If you wish to test for chloride when both bromide and iodide are present, first remove the iodine by precipitating with copper sulphate and sulphurous acid and filtering, or by distilling with iron ammonium sulphate. Then evaporate the solution containing the bromide and chloride to dryness, mix the residue with an equal quantity of potassium dichromate, add concentrated sulphuric acid, and distill. A red gas escapes (?). Conduct this gas into a little sodium hydroxide, which becomes yellow (?); the yellow color is proof that chlorine was present in the substance examined. Could bromine escape in this reaction? Would bromine color the sodium hydroxide yellow?

7. POTASSIUM OXALATE (NEUTRAL OR SECONDARY OXALATE).

When heated, the crystals lose water and crumble; heated higher, the salt evolves a colorless and inodorous gas, which, when lighted, burns at the mouth of the tube with blue flame (?). The residue in the tube has a grayish color, from a little carbon which has separated. Dissolve the residue in water, filter, and test the behavior of the filtrate with litmus paper, acids, and calcium chloride (?).

Page 22, lines 15 and 16, and again in line 19, instead of "sodium hydroxide" read *ammonia.*

What is the composition of the crystalline salt? of the dehydrated salt? of the residue after heating?

Potassium oxalate is easily soluble in water; reaction of the solution (?); if a little oxalic acid be added to the concentrated solution, after a few moments a new salt is precipitated, less soluble than the first; and of acid reaction and taste. This is acid or primary potassium oxalate. If much oxalic acid or mineral acids (?) be added to the solution of the neutral oxalate, the still less soluble peracid salt (potassium quadroxalate, $C_2O_4HK + C_2O_4H_2$) is precipitated, which contains to one equivalent of potassium four equivalents of oxalic acid (?).

If the concentrated solution of the neutral oxalate be mixed with the same volume of a saturated solution of sodium chloride and shaken, in a short time sodium oxalate is precipitated in the form of a crystalline powder. The oxalates of the alkali metals are soluble in water, as are ferric, chromic, and stannic oxalates and aluminium oxalate. All other oxalates are nearly or quite insoluble in water; consequently the solution of potassium oxalate forms precipitates with the salts of the alkaline earths and with the salts of most of the heavy metals. All these precipitates are soluble in mineral acids, but not in acetic acid.

Calcium chloride is precipitated as white, finely divided calcium oxalate, insoluble in water, ammonia and ammonium chloride, soluble in hydrochloric and nitric acids, but slightly soluble in acetic acid. Calcium oxalate is fully precipitated from its solution in hydrochloric acid by ammonia, and almost entirely precipitated by sodium acetate (?).

Dissolve two or three grams potassium oxalate in 200 cc. hot water, and add lead acetate slowly till a further addition causes no more precipitation; filter; wash the precipitate with water; bring it with the aid of a jet of water into a flask; add hot water and shake the flask; conduct sulphuretted hydrogen gas into this mixture. To test whether enough sulphuretted hydrogen has been used, close the mouth of the flask with the thumb; shake the flask violently for a minute and smell it; if the liquid retains the odor of the gas, enough has been used. Filter, and evaporate the colorless filtrate in a porcelain dish until only 4 to 5 cc. remain. On cooling, oxalic acid separates in crystals; take them from the liquid, lay them on filter paper and dry. Examine the acid as to taste, reaction, behavior when heated with carbonates, composition of the crystallized acid (?). How is oxalic acid manufactured?

Heat gently oxalic acid or potassium oxalate with concentrated sulphuric acid in a test tube. A gas is evolved; the mixture does not become black; the gas is colorless and inodorous, and burns, when lighted, with a blue flame (?). Conducted into barium hydroxide it forms a white precipitate (?).

A solution of oxalic acid, or a solution of potassium oxalate to which dilute hydrochloric, sulphuric, or nitric acid has been added, when treated with an oxidizing agent (manganese dioxide, lead peroxide, or potassium permanganate) develops a colorless and inodorous gas which precipitates barium hydroxide, but will not burn or support combustion (?). If enough

oxidizing agent be used, all the oxalic acid is decomposed.

9. SODIUM CARBONATE.

Freshly crystallized, it forms clear, transparent crystals which, exposed to the air, lose water and their transparency, and become gradually pulverulent. Composition of the crystallized (?) and of the pulverulent salt (?).

The salt melts in its water of crystallization when very gently heated. The water of crystallization escapes in part on heating further, and a salt containing less water separates. On heating higher still, all the water of crystallization is driven off, and dehydrated sodium carbonate (calcined soda) remains, which melts at a still higher temperature, and on cooling forms a crystalline mass.

Sodium carbonate is easily soluble in water, but not in alcohol. Crystallization from solution in hot water (?). Taste (?). Reaction (?).

Bring the salt on a platinum wire into the flame: it colors the flame yellow. Look at the flame through cobalt glass; the yellow color disappears.

Sodium salts are all soluble in water; sodium silicofluoride and sodium pyro-antimoniate are difficultly soluble in water.

Add to one drop of sodium carbonate on a watch-glass one drop of hydrochloric acid and three drops of platinum chloride; evaporate slowly, but not quite to dryness. From the concentrated solution crystals of sodium-platinum chloride (?) separate on cooling, easily soluble in water and in alcohol; (separation of sodium compounds from potassium compounds).

Sodium carbonate effervesces with acids; the gas evolved is colorless and inodorous; forms no vapor with ammonia; colors blue litmus paper wine-red; is much heavier than air; does not support combustion, and forms a precipitate with barium hydroxide which is soluble in acids.

The carbonates of the alkali metals are soluble in water; the carbonates of all other metals, excepting some bicarbonates (acid or primary carbonates), are insoluble in water; hence sodium carbonate precipitates solutions of almost all other metals. These precipitates belong to one of three classes: 1st. Neutral carbonates (examples Ca, Ba, Sr, Ag); 2d. Basic carbonates (Mg, Zn, Cu); 3d. Hydroxides (ferric salts, aluminium salts). Formulate these reactions. In the second and third cases carbon dioxide is set free, which escapes as gas on heating.

Those carbonates which are insoluble in water are soluble in acids. Some carbonates are soluble in carbonic acid, forming bicarbonates (Ca, Mg) (?).

10. DISODIUM PHOSPHATE (SECONDARY SODIUM PHOSPHATE), $PO_4Na_2H + 12H_2O$.

The crystals contain much water of crystallization, and crumble when long exposed to the air; the salt melts in its water of crystallization, and if not heated too strongly, the anhydrous (?) salt, PO_4Na_2H, remains when the water is driven off. This anhydrous salt

when heated higher gives off more water (?) and finally melts.

The melted salt is viscous and therefore forms, when heated with the blowpipe on charcoal, a drop or bead, while most alkali salts when melted spread over and sink into the pores of the charcoal. Add a drop of cobalt nitrate to this bead and melt again; the bead becomes blue (?).

The salt is easily soluble in water; when the hot solution cools, crystals separate; the solution has an alkaline reaction, although the salt is a so-called "acid" salt. What is meant by an acid salt (?).

Heated with concentrated sulphuric acid, no gas is evolved, because a very high heat is required to volatilize phosphoric acid.

Of the diphosphates and triphosphates (?), only those of the alkali metals are soluble in water; hence, although the other phosphates are soluble in acids, they generally separate again when the acid solution is neutralized (?) with an alkali (?). The monophosphates (?) are mostly soluble in water.

Sodium diphosphate forms white precipitates with barium, calcium, and strontium salts.

Magnesium sulphate is not precipitated by sodium diphosphate unless the solutions are very concentrated; if ammonia and ammonium chloride are added, a white crystalline precipitate of ammonium magnesium phosphate is formed (?). Water dissolves traces of this salt, but in ammonia and water it is quite insoluble; it is easily soluble in acids, even in acetic acid, and if the acid solution be neutralized with ammonia, it is again precipitated. Composition of this precipitate (?); behavior when heated in a tube (?).

Add *ferric chloride* to the solution of disodium phosphate; a yellowish white precipitate is formed (?). At the same time the reaction of the solution becomes acid (?). The precipitate is easily soluble in mineral acids (?), but not in acetic acid; hence it can be reprecipitated from its solution in acids by adding sodium acetate (?).

Silver nitrate forms with disodium phosphate a yellow precipitate (?); filter and test the reaction of the filtrate; the precipitate is easily soluble in nitric acid (?) and in ammonia (?); from the solution in nitric acid it can be reprecipitated by ammonia (?); from the solution in ammonia, by nitric acid (?). Phosphates which are insoluble in water (test with ammonium magnesium phosphate) are turned yellow by silver nitrate.

Add one drop of disodium phosphate to 2 cc. of the solution of ammonium molybdate in nitric acid; the solution turns yellow; heat it slightly, and a yellow precipitate of ammonium phospho-molybdate is formed $[(NH_4)_3PO_4(MoO_3)_{11}+6H_2O]$. Filter, wash the precipitate with water, dissolve it in ammonia, and precipitate the phosphoric acid by adding magnesium sulphate and ammonium chloride.

Add to a few drops of disodium phosphate two grams of tin and about 20 cc. nitric acid; heat on the water bath till all the tin is changed into a white powder; evaporate the excess of acid. Add hot water, filter, and wash the residue with hot water; the phosphoric acid is in the residue (?); test the filtrate for phosphoric acid;

dissolve the residue in ammonium sulphide; filter, and precipitate the phosphoric acid from the filtrate with a mixture of magnesium sulphate, ammonium chloride and ammonia.

Dissolve the *fused disodium phosphate* in water; the solution forms with silver nitrate a white precipitate (?), with ferric chloride a white precipitate (?) which is soluble in an excess of the alkaline phosphate (ferric pyrophosphate solution); gently heated with a solution of ammonium molybdate in nitric acid, the sodium pyrophosphate forms no precipitate; after boiling or heating for some time, a yellow precipitate is formed.

Secondary ammonium sodium phosphate, also called *microcosmic salt*, ($PO_4HNaNH_4 + 4H_2O$), crystallizes on cooling from a solution of six parts disodium phosphate and one part ammonium chloride in two parts boiling water (?); purify it by recrystallization (?); when heated it loses first the water of crystallization, then ammonia, then its basic water (?); the melted residue (?) dissolves most metal oxides (?); some oxides give the melted bead characteristic colors; hence the use of microcosmic salt as a reagent in blowpipe analysis.

Heat some microcosmic salt on the platinum foil until the melted residue no longer effervesces; after cooling, dissolve in water. This solution forms with silver nitrate a white precipitate (?); with a mixture of magnesium sulphate, ammonium chloride and ammonia, no precipitate; toward ammonium molybdate it behaves like sodium pyrophosphate.

[Acidulated with acetic acid and added to a solution of albumen, it coagulates the albumen.]

11. SODIUM SULPHITE.

When heated, it loses water of crystallization without melting. Dehydrate the salt by heating gently in a porcelain dish; heat the dehydrated salt higher in a tube; it softens and assumes a dark color; when cooled the fused mass is yellow; its aqueous solution has an alkaline reaction (?); test its behavior with a silver coin, with lead acetate, with sodium nitro-prussiate, with acids (?); (it should become clouded and give off hydrogen sulphide when warmed with an acid).

The alkaline salts of those oxygen acids of sulphur which contain less oxygen than sulphuric acid, are all decomposed by fusing; in this decomposition as much sulphate is always formed as the quantity of oxygen contained in the original salt can furnish. Deduct this amount of sulphate from the formula expressing the composition of the salt, and the subtrahend will be the formula for the decomposition product formed beside the sulphate. Write the equation for the decomposition of sodium sulphate (Na_2SO_3).

Sodium sulphite is easily soluble in water; the solution has an alkaline reaction and cooling taste with a flavor of sulphur.

Concentrated sulphuric acid or hydrochloric acid added to the salt causes effervescence (?). The gas evolved has the odor of burning sulphur. If dilute acids be used, the gas is not evolved till the solution is warmed (?).

Sulphurous acid, or more correctly, sulphur dioxide, is evolved when sulphuric acid is reduced (?); for

example, when concentrated sulphuric acid is heated with charcoal (?), sulphur (?), copper (?), silver (?), mercury (?) and other metals. It is absorbed abundantly by water. Prepare an aqueous solution of sulphurous acid by warming some copper foil in a flask with concentrated sulphuric acid and conducting the gas evolved into distilled water. Sulphurous acid is an energetic reducing agent (?). Added to potassium bichromate, the red solution instantly becomes green (?). Black lead peroxide becomes white (?). Manganese peroxide dissolves in it (?). Ferric salts lose their color and are reduced to ferrous salts (?).

Add a little sulphurous acid to a solution of mercuric chloride and heat gently; mercurous chloride is precipitated (?); add an excess of sulphurous acid and continue to heat; metallic mercury is precipitated as a gray powder (?). Concentrated nitric acid is reduced by sulphurous acid to nitric oxide (?). Chlorine, bromine and iodine (the last only in very dilute solution) are changed into their hydrogen compounds (?) by the action of sulphurous acid (?).

The solution of sodium sulphite forms a white precipitate with barium chloride, soluble in cold dilute hydrochloric acid, but generally not quite soluble because the sodium sulphite usually contains as impurity more or less sodium sulphate. Sulphurous acid, too, dissolves the barium precipitate (?).

Filter the acid solution of the barium precipitate if it is not clear; add bromine water to the filtrate; a white precipitate is formed (?).

Freshly prepared aqueous sulphurous acid forms no precipitate (?), or a very light precipitate (?), with barium chloride; but an addition of ammonia (?) or bromine water (?) causes a precipitate.

Sulphurous acid, as has been seen, combines readily with oxygen, forming sulphuric acid; but it also gives up its oxygen with comparative ease, as the following reactions will show, for which take aqueous sulphurous acid, or an aqueous solution of sodium sulphite to which dilute hydrochloric acid has been added.

Conduct hydrogen sulphide into the solution; sulphur is precipitated (?).

Mixed with zinc and hydrochloric acid, the solution evolves hydrogen sulphide (?); (tests: odor, lead paper).

Warm the solution with stannous chloride and hydrochloric acid; yellow stannic sulphide is precipitated (?).

If in the last two reactions a drop of copper sulphate solution be added, black copper sulphide is precipitated. This is a delicate test for sulphurous acid (?).

How is sulphurous acid prepared commercially, and how is it transformed into sulphuric acid?

With many coloring matters sulphurous acid forms colorless compounds; for example, with the coloring matter of most flowers; if dipped into dilute acid the coloring matter appears again. Use of sulphurous acid for bleaching woolen and silk goods (?).

Sulphurous acid has an antiseptic action (?). It is used for preserving wine and beer (?).

12. SODIUM HYPOSULPHITE, $S_2O_3Na_2 + 5H_2O$.

It melts in its water of crystallization, and when this is evaporated by gentle heat, it becomes solid again. Melt the dehydrated salt in a tube; it melts to a nearly black liquid, and forms, when cooled, a yellowish brown mass. This behaves like that obtained by heating sodium sulphite, except that, if acids be added to the aqueous solution, a voluminous precipitate of sulphur is formed. The decomposition resembles that of the sulphite. Write the equation according to the rule given in the preceding chapter. At the same time that the salt decomposes as expressed in the equation, a little free sulphur escapes; this partly sublimes in the tube and partly burns to sulphur dioxide; if the salt were not quite dehydrated, a slight odor of sulphuretted hydrogen is noticed. It may be said that the hyposulphites when heated behave like sulphite + sulphur; in all their reactions it will be seen that these salts behave like sulphites + sulphur; so, too, in their composition and in their formation. They are formed by the action of sulphur upon alkaline sulphites.

A hydrate (?) or anhydride (?) corresponding to the salts is not known; if the acid be set free by adding a stronger acid (HCl, SO_4H_2), it at once decomposes in heated concentrated solution, more slowly in cold dilute solution, into sulphur dioxide, sulphur and water (?).

Add hydrochloric acid to the dilute solution of the hyposulphite; at first it remains clear, but soon becomes opalescent, and has the odor of sulphurous acid. This is a characteristic reaction of all hyposulphites.

With oxidizing agents the hyposulphite behaves like the sulphite. Test this by suitable reactions; chlorine water or hypochlorites oxidize all its sulphur to sulphuric acid (?) (*antichlorine* in bleaching)? By iodine and water it is *not* oxidized to sulphuric acid, but forms sodium tetrathionate (?).

Sodium hyposulphite forms a white precipitate with barium chloride (?), soluble in much water.

With *silver nitrate* a white precipitate of silver hyposulphite is formed; heat gently; the color changes rapidly, becomes yellow, brown, and at last black; the silver hyposulphite and the elements of water are decomposed, forming black silver sulphide and sulphuric acid; test the reaction of the solution; filter, and prove the presence of sulphuric acid in the filtrate. Cupric salts behave similarly, copper sulphide being precipitated on boiling; so do lead and mercuric salts, though the decomposition is not so rapid (?). Mercurous nitrate yields at once a black precipitate (?). Stannous chloride a brown precipitate of stannous sulphide (?).

The hyposulphites of the heavy metals, insoluble in water, are soluble in an excess of sodium hyposulphite, forming double salts; other salts of the heavy metals insoluble in water are soluble in sodium hyposulphite solution forming double salts; for example, silver chloride, bromide, iodide—(use of this reaction in photography) (?)—mercurous chloride, lead sulphate.

With zinc and hydrochloric acid the hyposulphite behaves like the sulphite (?).

Alkaline hyposulphites are formed by the action of sulphur on alkali oxides. The so-called liver of sulphur

(*hepar sulfuris*), made by dissolving sulphur in sodium hydroxide or calcium hydroxide, or in the dry way by melting sulphur with alkali carbonates at moderate heat, contains sulphides and hyposulphite (?). Dissolve sulphur in boiling sodium hydroxide; behavior of the solution with acids (?) (*lac sulfuris*).

To test for hyposulphite in the presence of sulphides, precipitate the dilute solution with a solution of zinc sulphate; sulphur and zinc sulphide are precipitated, the hyposulphite remains in solution; filter, and test for it (?), or, add to the concentrated solution of the 'hepar' an excess of alcohol; the hyposulphite is precipitated and the sulphide remains in solution.

13. BORAX (SODIUM TETRABORATE), $B_4O_7Na_2 + 10H_2O$.

Large colorless monoclinic prisms, not efflorescent, with sweetish alkaline taste and alkaline reaction, easily soluble in water, insoluble in alcohol.

Heated on the platinum wire, or charcoal, the salt puffs up, loses its water of crystallization, and yields a white porous mass (calcined borax), which fuses at a higher heat to a vitreous colorless bead, which is not absorbed in the pores of the coal; in fusion the salt dissolves most metal oxides; (use of borax in soldering). These beads, double salts of boric acid with alkali and metal oxide, have sometimes characteristic color, often different in the oxidizing and reducing flames of the blowpipe; test this with cobalt, chromium, and manganous salts on the platinum wire.

Add to borax solution a few drops of concentrated sulphuric acid; a separation of crystalline boric acid follows; with other strong acids the same behavior.

Dissolve some borax in four times its volume of boiling water, add hydrochloric acid till the solution has an acid reaction, and let it cool. On cooling, boric acid, $B(OH)_3$, crystallizes in pearly scales, soluble in water and in alcohol. Filter off the crystals, press them between filter paper, dissolve a part in alcohol, pour into a porcelain dish and ignite; the solution burns with a green flame. (Characteristic reaction of boric acid.)

The same flame color is observed when a borate is powdered, mixed in a porcelain dish with concentrated sulphuric acid, alcohol added, and lighted; stir the mixture while burning; or, when a borate is brought in the loop of the platinum wire, moistened with concentrated sulphuric acid, and heated in the oxidizing flame of the blowpipe.

Moisten turmeric paper with an aqueous solution of boric acid; on drying, it is brown. For this reaction an aqueous solution of a borate to which enough hydrochloric acid has been added to cause an acid reaction may be used. (Characteristic reaction for borates.)

A concentrated borax solution gives with *barium* or *calcium chloride* a white precipitate of borate; both are soluble in acid, ammonia, or water, and in many salts. From the solution in excess of acids these borates are precipitated by adding an excess of ammonia; the precipitates are soluble, also, in an excess of the metal chloride which has been employed.

With ***magnesium sulphate*** no precipitate is formed; on boiling, magnesium borate, $Mg_3(BO_3)_2$, separates(?); on cooling, the precipitate dissolves again (?).

Silver nitrate yields with dilute borax solution a brown precipitate of silver oxide (?); with concentrated borax solution, a white precipitate of silver octoborate, $Ag_6B_8O_{15}$, colored somewhat yellow by silver oxide (?), soluble in nitric acid (?) or in ammonia (?).

14. AMMONIUM CHLORIDE (SAL AMMONIAC), NH_4Cl.

Heated in the tube, it volatilizes without melting, and condenses again in the cooler part of the tube, forming a crystalline crust (sublimation).

The ammonium salts of all volatile acids are volatile; either undecomposed as in the case of ammonium chloride, or with decomposition as is the case with the ammonium salts of the oxygen acids. The salts of the non-volatile acids lose the ammonia when fused (ammonium phosphate).

Taste, odor, solubility, reaction of NH_4Cl (?); crystallization on cooling the hot saturated solution (?).

Add to NH_4Cl solution NaOH and heat; [KOH, $Ba(OH)_2$, $Ca(OH)_2$ act in the same way]. The solution has the odor of ammonia; the NH_3 gas escaping from the solution forms vapors with a drop of HCl or NO_3H held on a stirring-rod over the solution (?). The gas colors red litmus paper blue, turmeric paper brown, and colors strips of paper which have been moistened with solutions of mercurous nitrate (?), copper sulphate (?), manganous sulphate (?).

If but little ammonium salt be present, it is a more delicate test to set the ammonia free, as follows: Mix a few drops of very dilute NH_4Cl solution with so much dry calcium hydroxide that the mass remains powdery; ammonia can be recognized at once by the odor, and by the formation of vapor with acid. The minutest traces of ammonia can be detected by mixing as above with calcium hydroxide in a small beaker, and covering the beaker with a watch-glass on the underside of which is a strip of moist red litmus paper or moist turmeric paper.

Mix some powdered NH_4Cl with four times as much dry $Ca(OH)_2$, bring into a flask, add water enough to make the mass pasty; warm gently; conduct the gas evolved into water, which absorbs it readily (at 0° centigrade 1050 volumes, at 15°, 730 volumes). This solution (ammonia, ammonium hydroxide) is lighter than water, has the odor of ammonia gas, has an alkaline reaction, and behaves with acids and salts like a "caustic alkali" (?).

It is a much used reagent; it is always employed when it is desired to neutralize an acid, or decompose a salt without adding a non-volatile substance to the solution under examination. If an acid be neutralized with ammonia, the ammonium salt of the acid is formed. Make ammonium sulphate and ammonium nitrate from the acid and ammonia; crystallize them by evaporation; test the behavior of the dry salts when heated (?).

With *copper sulphate* solution ammonia forms a blue precipitate (?), soluble in excess of ammonia.

Bromine water or *chlorine water* added to ammonia causes an effervescence (?).

Tartaric acid forms a crystalline precipitate in the concentrated solution of ammonia or of ammonium carbonate (?). Solutions of the other ammonium salts are not precipitated (or only after standing a long time) by tartaric acid; but if a little sodium carbonate is added they are precipitated (?); they are also precipitated by monosodium tartrate (?).

Platinum chloride behaves with ammonium salts as with potassium salts. The ammonium compounds of tartaric acid and of platinum chloride are isomorphous in crystalline form with the corresponding potassium compounds, and are similar in their composition and in their chemical behavior. By fusing these compounds and examining the residue after fusion, the ammonium compounds can easily be distinguished from those of potassium (?).

Aqueous ammonia absorbs sulphuretted hydrogen readily. (1) Conduct hydrogen sulphide into ammonia till fully saturated; ammonium hydrosulphide is formed. (2) Take two equal volumes of ammonia, saturate one with hydrogen sulphide, then mix it with the other part; this is ammonium sulphide, the common reagent (?). Test the behavior of both solutions with ferrous-sulphate, zinc sulphate, manganous sulphate; with (1) the precipitation is accompanied by evolution of hydrogen sulphide; with (2) it is not (?). Both solutions turn yellow when exposed to the air, in consequence of oxidation (?). The freshly prepared colorless solution evolves with acids hydrogen sulphide *without*, the yellow solution *with*, precipitation of sulphur. What is the difference between mono- and poly-sulphides? Between sulphides and hydrosulphides?

15. BARIUM CHLORIDE, $BaCl_2 + 2H_2O$.

Heated in a tube, it loses water and melts at a comparatively high temperature. On the platinum wire it colors the flame green after continued heating in the flame; moisten the wire and test the reaction; it is alkaline (?). Barium chloride has a bitter saline taste and is poisonous. Test its solubility in water (?), in alcohol (?); its reaction (?), crystalline form (?), composition of the crystallized salt (?).

Sodium hydroxide forms a voluminous white precipitate in the concentrated solution of $BaCl_2$, which dissolves for the most part on heating the solution; filter hot; on cooling, crystalline barium hydroxide separates. The insoluble portion of the precipitate was formed by impurities in the sodium hydroxide (?); wash it with water and examine it (?).

Ammonia does not precipitate $BaCl_2$; but if ammonia is added to the solution and it be allowed to stand exposed to the air, a precipitate forms (?).

Alkaline carbonates precipitate all barium from the solution as a white powder, soluble with effervescence in acids (?). To make the precipitation with ammonium carbonate complete, it is necessary to add ammonia and to heat gently (?).

Sulphuric acid or *sulphates* precipitate from soluble barium salts all barium as $BaSO_4$, insoluble in water, in dilute acids, and in alcohol. Alkaline carbonates do

not change $BaSO_4$ at ordinary temperature; if the sulphate is boiled with a solution of sodium carbonate for a few minutes, it is partly transformed into barium carbonate. The change is not complete because the sodium sulphate which is formed works in the opposite way (?) upon the barium carbonate. The change of $BaSO_4$ into $BaCO_3$ can be entirely prevented by boiling the sulphate with two parts of sodium carbonate and one part of sodium sulphate. On the other hand, the change can be made complete by boiling $BaSO_4$ with Na_2CO_3 a few minutes, pouring off the liquid and adding fresh Na_2CO_3 and again boiling; by repeating this operation twice the barium is entirely changed into carbonate which, on filtering and washing repeatedly with water, dissolves completely in hydrochloric or nitric acid. Why is it necessary to wash it so carefully? If $BaSO_4$ be melted with four parts of Na_2CO_3, or K_2CO_3, it is also completely decomposed (?).

Barium sulphate heated on the wire, or better, on charcoal, in the reducing flame, suffers change; moistened with water it gives an alkaline reaction (?); it blackens metallic silver (?). Moisten with HCl and heat again in the flame, a green color is noticed; on first heating the sulphate this was not the case (?).

Potassium chromate forms a yellow precipitate with soluble barium salts (?); potassium bichromate yields the same precipitate; the precipitate is insoluble in water, soluble in hydrochloric or nitric acid. For this reason the precipitation by potassium bichromate was incomplete, and if filtered, the filtrate yields, on adding ammonia, more yellow precipitate (?). Barium chromate behaves toward alkaline carbonates like barium sulphate; *strontium chromate* also precipitates barium salts.

Ammonium oxalate precipitates white barium oxalate, soluble in acids (?) Ammonia reprecipitates it from the acid solution (?).

Hydrofluosilicic acid precipitates barium silicofluoride, $SiFl_6Ba$, quite insoluble in alcohol, and not more easily soluble in dilute acids than in water.

Disodium phosphate forms: (1) With barium chloride solution *alone* a white flaky precipitate, and the liquid will show an acid reaction (?). Let it stand for ten minutes; the precipitate will become crystalline, and now the liquid has a neutral reaction (?). (2) With barium chloride and ammonia, disodium phosphate forms a voluminous precipitate (?).

Both barium phosphates are soluble in water only in presence of ammonium salts, but are easily soluble in mineral acids and in acetic acid. Ammonia forms a voluminous precipitate from these acid solutions (?). Dissolve the barium phosphates (1) and (2), after carefully washing them with water, in nitric acid; (use as little acid as possible); precipitate them both with ammonia, and filter; the filtrate of (1) contains ammonium phosphate; the filtrate of (2) does not (?).

Concentrated HCl and NO_3H cause precipitates in barium salt solutions, soluble in water (?). $BaCl_2$ and $Ba(NO_3)_2$ are insoluble in alcohol.

Barium hydroxide is often used as a reagent. Its preparation from $BaCl_2$ is above described. Commercially it is prepared from the sulphate (?). It is

easily soluble in hot water, and crystallizes on cooling with water of crystallization: $Ba(OH)_2 + 8H_2O$.

On heating the crystals they melt in the water of crystallization, which at a high temperature escapes entirely, leaving the hydroxide, $Ba(OH)_2$, as residue; this loses no more water at the highest temperatures, but melts unchanged. $Ba(OH)_2$ has all the properties of a caustic alkali (?); its aqueous solution has strong alkaline reaction, and behaves towards acids and salts like sodium hydroxide, with the difference that many barium salts are insoluble in water. $Ba(OH)_2$ is used as reagent when a soluble alkaline base is required which may be easily removed by precipitation (?). All soluble barium salts are poisonous.

16. STRONTIUM CHLORIDE, $SrCl_2 + 6H_2O$.

Heated, the salt behaves like barium chloride, but it colors the flame dark red. Composition of the crystallized salt (?); solubility in water (?); in alcohol (?); reaction (?); form of crystals (?). The alcoholic solution burns with red flame.

$SrCl_2$ behaves towards KOH, NaOH, NH_3, Na_2CO_3, $Na_2C_2O_4$, and Na_2HPO_4, like $BaCl_2$.

Barium hydroxide precipitates concentrated solutions of strontium salts. The precipitate dissolves in water on heating.

Dilute sulphuric acid forms with $SrCl_2$ so voluminous a precipitate that the solution seems to have become solid; after a few moments—still sooner when heated—the precipitate takes the form of a white powder. If the solution of strontium salt be very dilute, or if the sulphuric acid or sulphate used as reagent be very strongly diluted with water (aqueous calcium sulphate solution), some minutes elapse before a precipitate appears. Strontium sulphate is somewhat soluble in water, still more soluble in dilute HCl or NO_3H, less soluble in dilute SO_4H_2, insoluble in alcohol or in a solution of ammonium sulphate. Alkaline carbonates or ammonium carbonate transform it completely into carbonate without heating, if it stands twelve hours; if boiled with sodium carbonate it is fully transformed in ten minutes; this transformation is not prevented by the presence of alkaline sulphate, as K_2SO_4 or Na_2SO_4 do not act upon $SrCO_3$.

Potassium dichromate does not precipitate strontium salts; potassium chromate only when the solution is concentrated; a solution of strontium chromate can of course not precipitate strontium salts, but does precipitate barium chromate from barium salts.

Hydrofluosilicic acid does not precipitate strontium salts.

Strontium nitrate is almost insoluble in alcohol; in a mixture of equal parts of alcohol and ether quite insoluble. If strontium chloride be repeatedly evaporated with nitric acid it is transformed into nitrate.

Strontium oxide and hydroxide behave in all reactions like the corresponding barium compounds, but the hydroxide is less soluble in water than $Ba(OH)_2$. In general the strontium compounds may be said to resemble strongly those of barium, with which they are mostly isomorphous (?).

What are the names, composition, and crystalline forms of the principal barium and strontium minerals (?).

17. CALCIUM CHLORIDE, $CaCl_2 + 6H_2O$.

The crystals contain more water of crystallization than barium chloride, and melt in their water of crystallization at a comparatively low temperature; the color imparted to the flame is yellowish red. $CaCl_2$ is isomorphous with $SrCl_2$. Dehydrated $CaCl_2$ is strongly heated by moistening with water (?). The crystallized $CaCl_2$ dissolves in water, with reduction of temperature (?); both deliquesce when exposed to the air (?); reaction (?); solubility in alcohol (?).

With *cold* calcium chloride solution, sodium carbonate forms a voluminous precipitate (?); freshly precipitated, this is soluble enough in water to react on litmus paper (?); it is still more soluble in ammonium salts. If it stands for an hour it becomes crystalline (?); it becomes crystalline much sooner on heating (?); when crystalline, it is insoluble in water or ammonium salts; if boiled with ammonium salts, however, it is gradually decomposed and dissolved (?); a solution of K_2SO_4 or Na_2SO_4 changes it neither at ordinary temperature nor on boiling. At high temperature $CaCO_3$ loses its carbon dioxide more readily than $BaCO_3$ or $SrCO_3$; test this with some small fragments of marble with the blowpipe; the residue (?), 'lime,' if moistened with a little water, crumbles, evolving heat, and forming a white powder, $Ca(OH)_2$, or 'slaked lime.' If this be again ignited it gives up its water easily and lime is again formed. Slaked lime mixed with much water and shaken forms the so-called 'milk of lime'; the clear aqueous solution of $Ca(OH)_2$ (prepare by shaking a little slaked lime with cold water and filtering) is called 'lime water'; both are used as reagents. $Ca(OH)_2$ is a strong (?) caustic (?) alkali. Although it is but slightly soluble in water, the solution, lime water, has a strong alkaline reaction.

Add to a dilute solution of sodium carbonate some milk of lime and shake the mixture; continue this till a sample of the filtered liquid poured into dilute acid no longer effervesces (?).

The filtered liquid has an alkaline reaction, and still keeps this reaction after mixing with a dilute $CaCl_2$ solution; while a solution of sodium carbonate mixed with enough $CaCl_2$ and warmed, no longer reacts alkaline (?).

Lime water exposed to the air gradually becomes clouded, more quickly if the breath is blown over its surface (?). Conduct carbon dioxide (marble and HCl) into lime water until the precipitate which first forms is dissolved (?). If this solution is exposed to the air it deposits all its lime slowly (if boiled, quickly) as crystalline precipitate (?). In what form do river and spring waters contain lime? Name the minerals which consist of $CaCO_3$? Dimorphism (?). Isomorphism with barium, strontium, and lead carbonates on the one hand, with magnesium, ferrous and manganous carbonates on the other (?).

Sulphuric acid and *sulphates* do not precipitate very dilute calcium salt solutions; in more concentrated

solutions a voluminous crystalline precipitate is formed; in quite concentrated solutions the precipitate absorbs the solution and forms a crystalline jelly; this precipitate contains water of crystallization, and does not become pulverulent by standing or when heated; it is somewhat soluble in water, still more in dilute HCl or NO_3H, insoluble in alcohol; it behaves toward alkaline carbonates like strontium sulphate; it differs from $SrSO_4$ in its greater solubility in water, which is increased by the presence of ammonium sulphate. $CaSO_4$ as mineral is either anhydrous (?) or contains water of crystallization (?). Calcined gypsum (?). Why does the mixture of calcined gypsum with water harden?

Sodium diphosphate forms a voluminous white precipitate in solutions of calcium salts (?). After a time it becomes less voluminous and crystalline (?). When first precipitated it is soluble in acetic acid; when it has become crystalline it is not; in HCl or NO_3H both are soluble (?); from this solution alkali hydroxides or carbonates precipitate tricalcium phosphate (?).

What are the most important minerals containing calcium phosphate? How are phosphoric acid and phosphorus manufactured from these materials? What is superphosphate? What is guano?

The insolubility of ferric phosphate in acetic acid is utilized to separate phosphoric acid from barium, strontium, calcium, and magnesium; neutralize the solution of the phosphate in HCl or NO_3H with sodium carbonate carefully; dilute with much water and add sodium acetate; add ferric chloride drop by drop until the liquid has a red color; heat till the liquid commences to boil, and filter hot; the filtrate contains the calcium, etc., but contains neither iron nor phosphoric acid. (This reaction will be more fully explained in the chapter on iron.)

Oxalic acid yields a white pulverulent precipitate of calcium oxalate; this precipitate is formed even in the most dilute solutions of calcium salts (such as aqueous SO_4Ca), is insoluble in water and in ammonium salts, soluble in NO_3H or HCl, almost insoluble in acetic or oxalic acid. The precipitation of a neutral calcium salt by oxalic acid is therefore incomplete; if filtered, the filtrate will yield with sodium acetate (?), ammonium oxalate (?), ammonia (?), a further precipitate. Neutral alkaline oxalates, however, precipitate all calcium from neutral solutions as oxalate (?). Calcium oxalate is reprecipitated from its solution in acids, completely by ammonia (?), almost completely by sodium acetate (?); boiled with Na_2CO_3, the oxalate is changed into carbonate.

Mix calcium oxalate with solutions of neutral chlorides or nitrates of the heavy metals [$CuCl_2$, NO_3Ag, $(NO_3)_2Pb$], and allow to stand in a warm place for an hour. Filter; the calcium will be found in the solution, the oxalic acid not (?). When heated, calcium oxalate first loses water; on heating higher, a gas escapes which burns with a blue flame (?). What is the residue?

Arsenious acid forms with lime water a white precipitate of calcium arsenite, very easily soluble in acids. Calcium salts, therefore, are not precipitated by arseni-

ous acid unless ammonia is added (?). In very acid solutions the precipitate forms slowly after the addition of ammonia, or does not form at all, because an excess of ammonium salt keeps it in solution.

With potassium, sodium, ammonium hydroxides, alkaline phosphates and chromates, and hydrogen silico-fluoride, calcium salts behave like strontium salts.

Crystallized calcium nitrate is easily soluble in alcohol, or in a mixture of equal volumes of alcohol and ether (separation from strontium).

Barium, strontium, calcium and magnesium form the group of the *alkaline earths*, so called because in their chemical conduct they stand between the alkali metals and the earth metals. With the alkaline metals they have the solubility and causticity of the hydroxides in common. In the insolubility of the normal (?) phosphates and carbonates they resemble the earth metals.

Magnesium stands much nearer the earth metals than the other three, which resemble each other closely in chemical conduct. Barium, strontium and calcium are separated from magnesium and the alkaline metals by ammonium carbonate to which ammonia and ammonium chloride are added; (the object of ammonium chloride is to retain the magnesium in solution). Their more important properties for analytical purposes are noted in the following table:

	Ba.	Sr.	Ca.
Hydroxides in cold water ...	Not easily soluble.	Soluble with difficulty.	Slightly soluble.
“ “ hot “ ...	More easily soluble than in cold.		Still less soluble than in cold.
“ at red heat......	Melts without decomposition.	Melts and loses water at high heat.	Does not melt and becomes easily anhydrous.
Carbonates at red heat......	Not decomposed.	Decomposed with difficulty.	Easily decomposed.
“ boiled with SO_4Na_2.	Changed to sulphate.	Not changed to sulphate.	
Sulphates in water and acids.	Insoluble.	Almost insoluble.	More soluble.
“ digested cold with $(NH_4)_2CO_3$......	Not.	Completely.	Completely
“ boiled with Na_2SO_4 and Na_2CO_3.....	Not.	Completely.	Completely transformed into carbonates.
“ boiled with Na_2CO_3	Incompletely.	Completely.	Completely
“ boiled with $(NH_4)_2SO_4$ solution.....	Not dissolved.	Not dissolved.	Dissolved.
Silico-fluorides in water and dilute acids	Soluble with difficulty.	Soluble.	Soluble.
Silico-fluorides in water and dilute acids with addition of alcohol	Insoluble.	Soluble.	Soluble.
Chlorides in absolute alcohol.	Insoluble.	Soluble on warming.	Easily soluble.
Nitrates in mixture ½ alcohol, ½ ether..................	Insoluble.	Insoluble.	Easily soluble.
REAGENT.			
SO_4Ca solution.........	Precipitation at once.	Precipitation after some time.	No precipitation.
SO_4Sr solution..........	Precipitation.	No precipitation.	No precipitation.
CrO_4Sr solution........	Precipitation.	No precipitation.	No precipitation.
Color of flame..............	Yellowish green.	Dark red.	Yellowish red.

In case all three metals are present, the flame colors appear one after another by heating for some time and occasionally moistening the wire with HCl. Sr is first seen; the dark red color flashes up and disappears again on bringing the wire slowly close to the flame. Then the calcium flame appears; hold the wire one or two minutes in the flame and the red flame gradually gives place to the green of the barium.

Separation.—Pour over the sulphates a concentrated solution of ammonium carbonate in ammonium hydroxide and let it stand twelve hours without heating; filter, wash carefully with water; heat with dilute NO_3H; filter the solution of Sr and Ca nitrates from $BaSO_4$; evaporate the solution to dryness; moisten the residue with a few drops of water, treat with a mixture of alcohol and ether (?). If you have a solution of the salts of Ba, Sr, and Ca, add sulphuric acid as long as a precipitate is formed; add ammonia without filtering until the solution is alkaline, then add the ammonium carbonate, and proceed as above. Another good method is to decompose the sulphates by boiling with one part Na_2CO_3 and three parts Na_2SO_4 thirty minutes. The separation of $SrCl_2$ from $BaCl_2$ with alcohol is less accurate.

18. MAGNESIUM SULPHATE.

Slender needles, unchanged by exposure to the air; melt when heated in the water of crystallization; when this is driven off, a white mass remains which requires high heat to fuse it. Heat it for some time on charcoal in the reducing flame ; the residue moistened turns red litmus blue, but does not blacken silver (?) ; moistened with cobalt nitrate and again heated with blowpipe, it assumes a reddish color.

Treated with soda on charcoal with reducing flame, Na_2S is obtained.

Solubility of $MgSO_4$ in water and in alcohol (?), reaction (?), taste (?).

KOH, NaOH, $Ca(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$, precipitate $Mg(OH)_2$ from Mg salt solutions ; the precipitate is voluminous ; almost insoluble in water, but enough to cause an alkaline reaction. In solutions of ammonium salts it dissolves readily (?). If, therefore, sufficient ammonium salt be added to a solution of magnesium salt, no precipitate is formed by NaOH in the cold ; but on boiling, $Mg(OH)_2$ is precipitated ; and with excess of alkali and continued boiling, all the magnesium is precipitated as hydroxide (?).

Mg salts and NH_4 salts combine, forming double salts which are not decomposed by ammonia ; therefore a mixture of Mg and NH_4 salts yields no precipitate with ammonia (?), neither does an acidulated solution of Mg salt (?). From the neutral solution of magnesium sulphate, ammonia precipitates one-half of the Mg as hydroxide, the other half remains in solution (?).

Sodium carbonate forms with Mg salts a voluminous precipitate of basic magnesium carbonate (?), insoluble in water, soluble in ammonium salts (?), and soluble in carbonic acid (?).

$MgSO_4$ solution mixed with an NH_4 salt remains clear when Na_2CO_3 is added, but on boiling a precipi-

tate is formed (?). The precipitation of the Mg salts with CO_3Na_2 in a cold solution is incomplete; filter from the precipitate and you will see that more basic carbonate separates from the filtrate(?). Precipitate some basic carbonate with Na_2CO_3 in boiling solution, filter, and wash the precipitate. Dried, it forms a very light white powder (*magnesia alba*).

Sodium bicarbonate forms no precipitate with a cold solution of Mg salt; on boiling, basic carbonate is precipitated; this dissolves in water into which CO_2 is conducted (?). On heating the solution, the basic salt is reprecipitated(?), but if the solution be allowed to stand at the ordinary temperature, crystalline neutral carbonate ($CO_3Mg + 3H_2O$) gradually separates.

CO_3Mg as mineral (magnesite) contains no water of crystallization, is isomorphous with calcite, and, unless powdered, is soluble with difficulty in acids.

When gently heated the basic carbonate loses water and carbonic acid and is changed into MgO. If you have not heated too strongly, on moistening the oxide with water, heat is evolved and the hydroxide $Mg(OH)_2$ is formed. When highly heated the oxide unites very slowly with water.

MgO is a strong base, which neutralizes the strongest acids, and precipitates most metals from their salts as hydroxides (?); heated with ammonium salts, dry or in solution, NH_3 is evolved (?).

Prepare $Mg(NO_3)_2$ by neutralizing NO_3H with basic magnesium carbonate and evaporating the solution; the salt crystallizes with difficulty [$Mg(NO_3)_2 + 6H_2O$]. It is deliquescent; on heating loses water;

highly heated, is changed into MgO. It is soluble in alcohol.

Prepare magnesium chloride by heating a mixture of MgO and powdered NH_4Cl in a covered porcelain crucible. It melts easily, and crystallizes on cooling; easily soluble in alcohol; deliquescent; from its aqueous concentrated solution $MgCl_2+6H_2O$ crystallizes. This melts on heating, loses water and HCl. After heating in a tube, is only partially soluble in water. After heating with the blowpipe on charcoal it is quite insoluble (?).

If the solution of $MgCl_2$ be evaporated with yellow mercuric oxide, or with silver oxide or carbonate, all magnesia is precipitated as hydroxide.

If $MgCl_2$ or $Mg(NO_3)_2$ be evaporated to dryness with oxalic acid, all HCl or NO_3H escapes; magnesium oxalate remains; high heat changes this into MgO (?).

Ammonium carbonate does not precipitate the cold dilute Mg salt solution; warmed, it becomes cloudy; if ammonium chloride be present it is not clouded. A concentrated solution of ammonium carbonate in ammonium hydroxide precipitates from the concentrated solution of the Mg salt, on standing, all Mg as crystalline ammonium-magnesium carbonate [$CO_3Mg CO_3(NH_4)_2+4H_2O$].

Disodium phosphate forms a precipitate (?) immediately only with very concentrated Mg salt solutions. In dilute solutions the precipitate first forms on heating; the liquid has an acid reaction (?). In presence of ammonium salt and free ammonia, disodium phosphate precipitates the Mg completely as ammonium-mag-

nesium phosphate ($PO_4MgNH_4+6H_2O$); the precipitate is at first voluminous, but soon becomes crystalline; in very dilute solutions it forms slowly; the precipitation is hastened by rubbing the glass with a stirring-rod; it is soluble in mineral acids and in acetic acid, and is reprecipitated from the acid solution by ammonia; it is but slightly soluble in water, quite insoluble in water containing ammonia, therefore the latter is used for washing it. What change occurs when the precipitate is sharply heated? The residue after heating is soluble in mineral acids; the solution prepared by the action of cold acid forms no precipitate with ammonia. When the acid solution is heated for some time the pyrophosphoric acid is completely changed into phosphoric acid, and now the solution can be precipitated with ammonia (?). By fusion with Na_2CO_3 the pyrophosphate is also changed into orthophosphate; ammonium-magnesium phosphate is easily decomposed by silver nitrate (?).

Ammonium oxalate yields only in concentrated solution of Mg salts, and after standing, a precipitate of magnesium oxalate; dilute solutions, especially if an excess of ammonium oxalate is present, are not precipitated.

How can you separate Mg from Ba, Sr, and Ca? How can you separate Mg from Na and K? How from ammonium compounds?

19. ALUMINIUM SULPHATE.

White crystalline mass; heated in a tube it melts, loses water, and acid vapors escape (?); heated upon charcoal, it leaves a residue of pure aluminium oxide free from sulphuric acid and sulphur, luminous when highly heated, infusible; moistened with cobalt nitrate and again sharply heated, it forms a blue infusible mass (?). Test the solubility of $Al_2(SO_4)_3$ in water (?), in alcohol (?); its reaction (?). Aluminium oxide is a very weak base; it does not fully neutralize even the weaker acids; hence all aluminium salts, even the basic salts, which are soluble in water, have an acid reaction. When the salts are ignited the acid escapes, unless it is like phosphoric acid, not volatile (?). Aluminium oxide does not decompose ammonium salts (?); with very weak acids, like carbonic acid, it forms no salts (?). But toward strong bases $Al(OH)_3$ behaves like an acid; it is soluble in caustic alkali, and when ignited with alkaline carbonates drives off CO_2, forming salts in which the aluminium oxide is the acid; these are called aluminates; by evaporating the alkaline solution these can be obtained in crystalline form, but not easily in small portions; for example, AlO_3Na_3, AlO_2Na. Some minerals are aluminates, as spinell $(AlO_2)_2Mg$, gahnite $(AlO_2)_2Zn$, chrysoberyl $(AlO_2)_2Be$; these are derived from the hydroxide AlO.OH. From solutions of aluminium salts, ammonia precipitates aluminium hydroxide, $Al(OH)_3$, as a colorless gelatinous mass, but slightly soluble in excess of ammonia; if the solution be heated until the odor of ammonia disappears, the precipitation is complete. Potassium, sodium, barium hydroxides also precipitate $Al(OH)_3$, but the precipitate dissolves easily in an excess of the reagent (?); if the alkaline solution be neutralized with an acid, $Al(OH)_3$ is again precipitated; an excess of acid dis-

solves it, and from the acid solution it can be precipitated by ammonia; ammonium salts also precipitate $Al(OH)_3$ from the alkaline solution (?), completely on heating a few minutes. If the alkaline solution be saturated with H_2S or CO_2, all $Al(OH)_3$ separates (?). $Al(OH)_3$ is colorless or white; when dried it forms a yellowish or greenish mass like horn; it is insoluble in water; when heated it loses water and forms aluminium oxide, Al_2O_3. This, if it has not been sharply ignited, is easily soluble in acid or alkali; but if it has been exposed to high heat, it is insoluble in acid or alkali, like the crystalline oxide occurring as mineral (corundum, sapphire, ruby, emery). By fusion with monosodium sulphate, or sodium carbonate or hydroxide, or by continued boiling with equal parts of concentrated SO_4H_2 and water, the Al_2O_3 may be dissolved (?). *Mono-* or *disodium carbonate* precipitates from Al salts $Al(OH)_3$ (?), but little soluble in excess of the disodium carbonate, still less in monosodium carbonate; *ammonium carbonate* behaves like monosodium carbonate.

Barium carbonate or *ammonium sulphide* precipitates all aluminium as hydroxide without heating (?). A solution of aluminium acetate decomposes with water on boiling, and all the aluminium is precipitated as $Al(OH)_3$ (?). Therefore, if we neutralize a solution of any aluminium salt with CO_3Na_2 as far as is possible without forming a precipitate, then add sodium- or ammonium-acetate and heat till the solution commences to boil, all the aluminium is precipitated as $Al(OH)_3$ (?); on cooling, the precipitate partially dissolves, and the more free acetic acid is present, the greater the amount dissolved.

Sodium phosphate precipitates voluminous aluminium phosphate (?), soluble in caustic alkali (?) but not in barium hydroxide; from the alkaline solution, which behaves toward acids and ammonium salts like sodium aluminate, barium hydroxide or chloride precipitates all phosphoric acid (?); the aluminium remains in solution. $AlPO_4$ is easily soluble in mineral acids, but not in acetic acid, therefore it can be precipitated from its acid solution by adding sodium or ammonium acetate (?).

$AlPO_4$ is soluble in $Al(C_2H_3O_2)_3$. Therefore, in a solution of an aluminium salt to which $C_2H_3O_2Na$ has been added, a small amount of PO_4Na_2H forms no precipitate.

Tartaric acid does not precipitate aluminium salts. Add to a solution of an Al salt, tartaric or citric acid (or any non-volatile organic acid) in sufficient quantity, and the aluminium will not be precipitated by ammonia, ammonium carbonate or sulphide, sodium hydroxide or carbonate. To prove the presence of aluminium in such a solution you must destroy the organic acid by evaporating the solution and igniting the residue. Al_2O_3 remains, which may be made soluble by one of the methods already described.

$AlPO_4$ behaves toward tartaric acid and ammonia like $Al(OH)_3$; from its solution in ammonia to which tartaric acid has been added, the phosphoric acid is completely precipitated by $MgSO_4$ (?); all the aluminium remains in solution; the PO_4MgNH_4 is, however,

generally impure, as basic magnesium tartrate is usually precipitated at the same time.

Aluminium chloride (how is it made?) is volatile and can be sublimed. If, therefore, a mixture of an aluminium salt and ammonium chloride is ignited, the aluminium is partially volatilized as chloride. Make a solution of $AlCl_3$ by dissolving $Al(OH)_3$ in HCl, or by decomposing $Al_2(SO_4)_3$ with $BaCl_2$; when the solution is sufficiently concentrated by evaporation, crystals of $AlCl_3 + 6H_2O$ form: these are deliquescent, soluble in alcohol, and on heating lose water and HCl; a residue of Al_2O_3 with a little basic chloride remains.

The metals of the

ALKALIES	ALKALINE EARTHS	EARTHS
Are monovalent (MX).	Are bivalent (MX_2).	Are trivalent (MX_3).
Decompose water and are oxidized by the air at ordinary temperature.		
Actively.	Slowly.	Not at all.
The hydroxides are in water		
Very easily soluble with strongest alkaline reaction.	Soluble, with decreasing ease from $Ba(OH)_2$, which is easily soluble in hot water, to $Mg(OH)_2$, which is scarcely soluble. Alkaline reaction.	Quite insoluble. No reaction on vegetable colors.

The sulphides in contact with water

Are dissolved without decomposition. Alkaline reaction.	Are dissolved with alkaline reaction and partial decomposition: $2BaS + 2H_2O = Ba(OH)_2 + Ba(SH)_2$; CaS is almost insoluble; MgS is completely decomposed.	Are completely decomposed: $Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S$.

The carbonates are in water

Easily soluble with alkaline reaction.	Insoluble.	The oxides of the earth metals do not unite with CO_2.
When the carbonates are heated they		
Do not lose CO_2.	Lose CO_2 with increasing ease from Ba to Mg.	

The chlorides at high heat are by steam

Not decomposed.	Partially decomposed.	Fully decomposed.

20. SODIUM SILICATE (WATER GLASS).

Semi-transparent non-crystalline substance. It fuses to a transparent bead, which is colored by metallic oxides like borax.

Fragments do not appear to dissolve in water, but the solubility is shown by the taste (?) and reaction (?) of the substance; reduce it to an impalpable powder and you will see that it dissolves slowly in water. The addition of a few drops of sodium hydroxide hastens solution. (Try with 5 grams of the salt and 100 grams of water.)

The solution concentrated by evaporation forms when cold a jelly-like mass, easily soluble in boiling water. Add acid to the concentrated solution; white voluminous normal silicic acid is precipitated (?); after standing some time, dilute solutions form the precipitate as a transparent jelly. Once separated, the silicic acid is insoluble in water and in acids, but the separation is not complete. To separate the silicic acid completely, add acid to the solution till the reaction is decidedly acid, and evaporate to dryness; treat with water, which dissolves the alkali as salt of the acid used, and a white insoluble tasteless powder, SiO_2, remains. This is insoluble in all acids except hydrofluoric acid. Even fused phosphoric acid does not dissolve it. Make a bead of microcosmic salt on a platinum wire and bring a fragment of the silicate into the bead, and fuse for a few moments; the base combined with the silicic acid is dissolved (?); the latter is insoluble, and can be observed as a white mass in the bead (characteristic reaction of silicates). Hydrofluoric acid dissolves silicates, but decomposes them (?). When heated, if the silicic acid is pure, the whole solution is volatilized. This must be tried in a platinum vessel, not in glass or porcelain; why? Hydrofluoric acid also decomposes those silicates which cannot be dissolved by other acids; take a fragment of glass, reduce to fine powder, add hydrofluoric acid and a little concentrated sulphuric acid, evaporate until part of the SO_4H_2 escapes, analyze the residue (?); what has become of the silicic acid? In sodium or potassium hydroxide, silicic acid is soluble; that precipitated from silicates by acids easily, those forms which occur in nature more slowly, the amorphous more quickly than the crystalline. By fusion with sodium and potassium hydroxides or carbonates, barium hydroxide, or the carbonates of the alkaline earths, silicic acid or silicates are transformed into silicates soluble in acid (?). All silicates excepting those of the alkali metals are insoluble in water. Hence sodium silicate yields precipitates with all metal salts; these consist of double silicates of sodium and the metal, and are mostly soluble in dilute NO_3H or HCl. Such mixed silicates are very common in rocks and minerals. Name some with and without water of crystallization (?). Name silicates decomposable by acids (?). Others which acids will not decompose (?).

Silicic acid does not combine with ammonia; the solution of sodium silicate behaves toward ammonium salts (chloride, sulphides) as towards acids (?).

21. CALCIUM FLUORIDE (FLUORSPAR).

Fuses on charcoal, forming a transparent bead; on long-continued heating the mass becomes luminous and infusible (?). When cool, moisten with water; it shows alkaline reaction (?). Powder some fluorspar and heat in a test tube with concentrated SO_4H_2: a gas escapes (?); a drop of $AgNO_3$ on a stirring-rod held in the escaping gas is covered with a white coating which does not dissolve in ammonia (?); a drop of distilled water behaves like the NO_3Ag (?); at the same time the glass of the test tube is corroded, as will be seen by washing and drying it. Mix $CaFl_2$ in a platinum

crucible with conc. SO_4H_2, stir the mixture so that it forms a thin paste; coat a watch-glass with wax or paraffin; draw lines through the wax coating; cover the crucible with the glass, and let it stand for half an hour in a warm place. Remove the wax; the lines drawn will be etched on the glass (?).

Mix 20 grams fluorspar with 20 grams powdered glass; bring into a flask; add enough conc. SO_4H_2 to form a half-liquid paste, and warm; conduct the escaping gas (?) through a tube bent twice at right angles into a flask of a capacity of 500 cc. in which are 100 cc. water; the conducting tube must not quite touch the surface of the water; shake this flask often enough to keep the inner surface wet; increase the heat slowly till the SO_4H_2 commences to boil; then disconnect; the water in the large flask will be filled with white clots of precipitate; filter and examine them (?). Evaporate the acid filtrate (?) in a porcelain dish to one-fourth its volume. With this solution of hydrogen silico-fluoride make the following tests: A drop evaporated on a watch-crystal leaves a spot which water will not remove (?). Neutral or acid potassium salt solutions form with hydrofluosilicic acid a gelatinous precipitate; it is at first so transparent that it is hard to see, but gradually settles; add to the mixture an equal volume of alcohol; the precipitate becomes white and dense; if enough $SiFl_6H_2$ be used, all potassium is precipitated; filter and wash with alcohol; boil a part of the residue with water; it dissolves with acid reaction; ignite the dried salt in a covered platinum crucible; it is changed into potassium fluoride (?); you will note a coating of SiO_2 on the inner side of the cover (?). Potassium fluoride is soluble in water.

Sodium salts behave in the same way with $SiFl_6H_2$. Ammonium salts are not precipitated.

How does $SiFl_6H_2$ behave with salts of the alkaline earths?

If hydroxides or carbonates of the alkalies are added to $SiFl_6H_2$ till the solution has an alkaline reaction, it is decomposed (?).

Add an excess of ammonia to the remainder of the $SiFl_6H_2$; $Si(OH)_4$ is precipitated (?); evaporate the mixture to dryness on the water-bath without filtering; treat the residue with water; what dissolves? SiO_2 remains undissolved. The solution gives no precipitate with NO_3Ag; AgFl is soluble in water. With the salts of the alkaline earths, ammonium fluoride forms voluminous precipitates (?); the precipitate with calcium chloride (?) is a gelatinous mass; add ammonia and warm, it becomes denser and can be filtered; it is soluble in HCl or NO_3H, and cannot be precipitated from the acid solution by ammonia, because it is soluble in ammonium salts.

22. POTASSIUM DICHROMATE.

The salt is anhydrous, fuses when heated, cools, forming a crystalline mass, which then crumbles; highly heated it decomposes, evolves a gas (?), and leaves as residue a mixture of chromic oxide and potassium chromate (?). Solubility (?), reaction (?), crystallization from hot solution (?). It is poisonous.

Pour a solution saturated at ordinary temperature into 1½ times its volume of concentrated SO_4H_2. On cooling, red needles of chromic anhydride, CrO_3, separate. Filter through glass wool with the aid of a filter pump. The anhydride is very soluble in water; its solution in little water is yellowish red, and destroys organic substances (paper) like conc. SO_4H_2. The dilute solution is yellow, tastes sour, colors litmus red and bleaches it on drying (?).

Add to the red solution of $Cr_2O_7K_2$, NaOH, or Na_2CO_3, it becomes yellow (?); add an acid to this solution, it turns red (?). Potassium chromate, CrO_4K_2, is yellow; in composition and crystalline form isomorphous with potassium sulphate. *Barium chloride* yields with $Cr_2O_7K_2$ a yellow precipitate (?), insoluble in water, easily soluble in dilute HCl or NO_3H and in chromic acid; CrO_4K_2 gives the same precipitate (?).

The chromates of the heavy metals are mostly insoluble in water and dilute acids.

Lead chromate (chrome yellow) (prepare with lead acetate and $Cr_2O_7K_2$) is insoluble in acetic acid, soluble with difficulty in dilute nitric acid, easily soluble in NaOH (?). Warm it with ammonia, or with insufficient NaOH for solution. It turns red (?) (chrome red), while the supernatant liquid turns yellow (?).

Dark red silver chromate, dark red mercurous chromate, light red mercuric chromate, are precipitated by adding $Cr_2O_7K_2$ to the respective nitrates. Fuse the mercury chromates; a residue of green chromic oxide remains (?).

Heat a dry chromate with concentrated sulphuric acid, a gas escapes (?). Heat a dry chromate with conc. HCl, a gas escapes (?). The color of the solutions changes from yellow through brown (intermediate chromic oxide) into green (?).

Chromic acid readily gives up some of its oxygen, hence acidulated chromate solutions easily become green (?) when reducing agents are added; for example, SO_2, H_2S, $SnCl_2$, alcohol, oxalic acid (?).

H_2S or $(NH_4)_2S$ forms in the neutral or acid solution of chromates a dirty greenish precipitate (?).

Ignite a mixture of dry potassium dichromate with an equal volume of sulphur or ammonium chloride; treat the cooled mass with water, the residue is bright green chromic oxide (?). Chromic oxide is a weak base, which in its chemical reactions strongly resembles aluminium oxide; its soluble salts have an acid reaction, and when ignited lose their acid if it is volatile (?). When crystallized they are mostly violet in color; a solution in *cold* water retains the same color. On *boiling* the solution the color changes to green (?). Let the solution stand for a long time, it will gradually become violet (?).

Prepare a solution of chromic oxide salt by boiling $Cr_2O_7K_2$ with HCl, adding a little alcohol (?) and evaporating on the water-bath; with NaOH it yields a grayish green precipitate of hydroxide (?) which dissolves in excess of NaOH with emerald green color (?); this solution, sodium chromite, behaves toward acids, ammonium salts, and H_2S like sodium aluminate; *boil* the dilute alkaline solution, $Cr(OH)_3$ is precipitated; (separation from Al).

In the alkaline solution the chromic oxide can be

easily oxidized to chromate; for example, by hypochlorites (?), chlorine or bromine water (?), potassium permanganate (?), lead peroxide; when the green color is changed to yellow the oxidation is complete; all Cr is now in the form of sodium chromate in solution and can no longer be precipitated by ammonium salts, but can be precipitated by lead acetate after acidulating the solution with acetic acid (?), or by mercurous nitrate after acidulating with NO_3H (?).

$Cr(OH)_3$ is somewhat soluble in ammonia with reddish color.

Secondary or primary alkali carbonates form a green precipitate (?). This contains carbonic acid, and dissolves with green color in a large excess of the carbonate.

Barium carbonate precipitates cold, on standing, all Cr as $Cr(OH)_3$. $(NH_4)_2S$ precipitates all Cr as hydroxide.

Tartaric acid behaves toward Cr salts as toward Al salts.

Continued ignition renders chromic oxide insoluble in acids. This oxide, and other insoluble chromium compounds, may be rendered soluble by fusion with monopotassium sulphate, or better, by fusion with saltpetre and sodium carbonate; the yellow fused mass (test for Cr) contains the chromium as soluble alkali chromate; (separation from oxides not soluble in alkaline solutions).

Chromium compounds form with microcosmic salt or borax a green bead in both oxidizing and reducing flame (?).

In what form does chromium occur in nature?

23. MANGANESE DIOXIDE (PYROLUSITE).

Black, crystalline; powder grayish black; it is the most important manganese material for technical purposes (?); heated in a tube it loses water and a gas escapes (?). The residue after ignition is manganous manganic oxide, Mn_3O_4. The same gas escapes on heating MnO_2 with conc. SO_4H_2; here manganic sulphate is first formed (?), then manganous sulphate (?). In *cold* HCl the finely powdered mineral dissolves slowly, forming a dark brown liquid (?) which slowly—when heated, quickly—evolves Cl and is reduced to $MnCl_2$, manganous chloride. Prepare this by warming in a flask 20 grams powdered MnO_2 with 200 grams com. HCl; conduct the escaping gas into a cold solution of 60 grams crystallized sodium carbonate in 200 grams water. When no more Cl escapes, boil the contents of the flask until the color has become brownish yellow (?), then evaporate to dryness in a porcelain dish, and dissolve the residue in water. Test the action of the solution of Cl in CO_3Na_2 with acids (?), litmus paper (red and blue) (?), indigo (?), lead acetate (?), manganous chloride (?), ferrous sulphate (?).

In what reactions do alkali chlorates and hypochlorites differ? How can you detect the presence of each in a mixture of both?

Sodium hydroxide precipitates all Mn from the $MnCl_2$ solution as manganous hydroxide (?), white, voluminous, insoluble in excess of alkali, soluble in ammonium salts (?). In its chemical behavior it resembles magnesium hydroxide, with the salts of which the manganous salts are mostly isomorphous.

Manganous oxide cannot be reduced to metal by heating in a current of hydrogen; the hydroxide or carbonate thus heated forms green anhydrous MnO; heated in air they form black Mn_3O_4 (?).

The manganous salts contain water of crystallization. Crystalline or in solution they are mostly of pink color; anhydrous they are colorless. They do not absorb oxygen from the air, and behave toward NH_3 and NH_4Cl like Mg salts, *excepting* that their solution in NH_3 absorbs oxygen from the air and gradually precipitates all manganese as manganic hydroxide (?), which is insoluble in NH_3.

Alkali carbonates and *oxalates* precipitate white carbonate or oxalate, soluble in ammonium salts; the oxalate is insoluble in acetic acid. Manganous nitrate, $Mn(NO_3)_2$ (prepared by dissolving the pure carbonate in NO_3H), evaporated to dryness and gently ignited, forms MnO_2 (?); if sharply ignited, Mn_3O_4. *Barium carbonate* does *not* precipitate cold manganous salts. *Sodium phosphate* precipitates white manganous phosphate, soluble in acids (?); from the acid solution NH_3 precipitates crystalline ammonium manganous phosphate (?) which turns brown when exposed to the air (?). H_2S does not precipitate neutral manganous salts (?); even manganous acetate, or a solution of manganous salt to which sodium acetate has been added, is not precipitated (?). $(NH_4)_2S$ precipitates reddish manganous sulphide (?), insoluble in NH_3 and NH_4Cl, easily soluble in mineral acids and in acetic acid. If the moist sulphide is exposed to the air it becomes brown, and on treating with water a part dissolves as manganous salt (?).

Manganic oxide (anhydrous as braunite, Mn_2O_3; with water of crystallization as manganite, $Mn_2O_3 + H_2O$) is a very weak base whose unstable salts are cherry red or purple in solution. The phosphate is the most stable; prepare it as follows: add a few drops of NO_3H to a manganous salt, add conc. phosphoric acid, and boil in a porcelain dish till the nitric acid begins to evaporate (reaction for Mn); Mn_2O_3 colors the microcosmic bead amethyst red. All Mn compounds form this bead in the oxidizing flame; in the reducing flame the bead is colorless (?).

Hydroxides of *manganese dioxide*, MnO_2, are formed when manganous salts are precipitated by alkali hydroxide in presence of an oxidizing agent; sodium hypochlorite (?), Br or Cl (?), potassium permanganate, form thus with manganous salt solutions brown precipitates of perhydroxides, $Mn(OH)_4$ or MnO_3H_2. From an acidulated (not strongly acid) solution of a manganous salt to which sodium acetate has been added, on warming with Br water (?) all Mn is precipitated as perhydroxide (?).

The *peroxide* has only weak basic properties (?); it is quite insoluble in dilute acids unless these have reducing power like sulphurous acid.

If dilute acid and a reducing agent are used together, the peroxide dissolves as manganous salt. Test this with dilute SO_4H_2 and ferrous sulphate (?) or alcohol (?) or oxalic acid (?).

Manganic oxide (?), *manganous manganic oxide* (?), and all *other oxides of* Mn *rich in* O (?), behave with conc. SO_4H_2, with HCl, with dilute acids and

reducing agents, like the peroxide; *all* are reduced to manganous salt, giving up their oxygen as oxygen, or yielding an equivalent amount of chlorine or doing an equivalent amount of oxidizing work (?). When heated exposed to the air, *all* these oxides yield the same final product, Mn_3O_4. Manganous oxide absorbs the necessary O from the air; the higher oxides lose their excess of O until the composition of the residue is Mn_3O_4.

Manganic acid. If any oxide of Mn be fused with caustic potash or soda, oxygen is absorbed from the air and dark green alkali manganate is formed. Owing to the intense color of alkali manganate, the least trace of Mn may be detected by fusing the powdered substance with CO_3Na_2 and a little NO_3K on the platinum foil; a trace of Mn imparts a bluish green color to the fused mass. Heat 5 grams KOH with 3 grams ClO_3K in a crucible, slowly, till the mass fuses, add 5 grams powdered manganese peroxide, and heat just enough to keep in fusion. The dark green mass dissolves in *little* water with green color, as potassium manganate, MnO_4K_2 (?). Add to half the solution more water; brown manganese perhydroxide is precipitated, and the color of the solution changes to a beautiful purple (?) (chameleon mineral). (This change of color is more rapid if the excess of alkali be partly neutralized by adding an acid, or by conducting CO_2 into the solution.) The solution now contains *potassium permanganate*, MnO_4K; this and *permanganic acid* are very energetic oxidizing agents and are frequently used as such. In *alkaline* or *neutral* solution the permanganate gradually becomes green (?) in consequence of loss of oxygen, and then, losing more O, it is precipitated as $Mn(OH)_4$ (?). In *acid* solution it gives up so much oxygen that it is reduced to manganous salt; test with ferrous sulphate (?), with oxalic acid (?).

Permanganic acid is soluble in water with purple color. When a solution of any manganese compound is warmed with NO_3H and lead peroxide, or minium, the faintest trace of manganese is shown by the formation of permanganic acid, which can be detected by the purple color of the solution. The test is best made as follows: Dilute about 5 cc. conc. NO_3H with an equal volume of water, add about a saltspoonful of minium, and heat to 60°–70°; now add *drop by drop* the *very* dilute solution of the substance to be tested; the first drop will usually produce the reaction. (The most delicate Mn test.) Why must this test be conducted in this way instead of adding the NO_3H and minium to the conc. solution of the substance to be tested?

24. IRON.

Is attracted by the magnet; infusible with blowpipe; treated with oxidizing flame, a black coating is formed (?); with non-oxidizing (?) acids, it evolves H, which, owing to contamination with hydrocarbons, has an unpleasant odor.

What are the differences between wrought iron, cast iron, and steel? Add a mixture of 50 grams conc. SO_4H_2 and 200 grams water to 30 grams iron filings in a flask; as soon as the effervescence slackens, heat

gently and then boil till no gas escapes, and a sample poured into a test tube crystallizes on cooling; filter into a porcelain dish in which are 3 grams conc. SO_4H_2, and allow it to crystallize 24 hours. Filter through fragments of glass, wash with a little cold water, spread the crystals on filter paper and let them dry. Taste (?); reaction (?); crystalline form (?); solubility in water (?), in alcohol (?); composition of the crystals (?); behavior when heated (?); when sharply heated (?); on heating in tube (?) and on platinum foil (?); behavior of aqueous solution exposed cold to the air (?); on boiling (?).

For the following tests use $FeCl_2$ prepared by boiling dilute HCl with an excess of iron; do not filter, but let it stand with the undissolved iron till used. *Alkaline hydroxides*, *calcium* and *barium hydroxides* form a voluminous precipitate (?), in the first moment greenish white, then darker, and on standing reddish brown (?) Boil a part of the mixture in a porcelain dish; the precipitate becomes black and pulverulent (?) (*Ethiops martialis*).

Ammonia forms the same precipitate, but incompletely; the filtrate contains ferrous salt, and on standing in an open vessel precipitates all iron as ferric hydroxide (?). If an excess of NH_4Cl be added to the ferrous salt and warmed, ammonia forms no precipitate (?) or a small black precipitate (?); the solution behaves in the same way if it contained much free acid before NH_3 was added.

Alkali carbonates precipitate from $FeCl_2$ ferrous carbonate.

H_2S forms in the neutral solution of ferrous salt a small black precipitate (?); acid solutions remain clear. If sodium acetate be added to the acid solution, continued addition of H_2S precipitates all Fe as FeS (?).

$(NH_4)_2S$ or H_2S in NH_3 solution precipitates fully (?); the solution above the precipitate is green from suspended precipitate, which is slowly deposited. An addition of NH_4Cl hastens this; filter and leave the residue on the filter; change on exposure to the air (?).

Potassium cyanide forms a reddish brown precipitate, soluble in excess of KCN on addition of a few drops of KOH or NaOH and warming; filter this solution from a little ferric hydroxide which is formed and add ferric chloride, it yields a blue precipitate.

Potassium ferrocyanide forms in solutions of ferrous salts a bluish white precipitate (?) which turns blue (Prussian blue) by exposure to the air or on treatment with oxidizing agents (?).

Potassium ferricyanide forms a dark blue precipitate (?); how does this precipitate behave on treatment with sodium hydroxide? *Potassium sulphocyanide* does not color the ferrous salt solution unless this contains traces of ferric salt; the mixture turns red on exposure to the air (?). *Barium carbonate* does not precipitate cold solutions of ferrous salts.

Oxalic acid forms in *concentrated* ferrous solutions a yellow precipitate (?) which from *dilute* solutions slowly separates in crystalline form; washed, dried, and heated to a red heat with air excluded, this pre-

cipitate yields black pyrophoric iron (?); heated exposed to the air, it yields iron oxide, black when heated, reddish brown on cooling (*colcothar; caput mortuum; rouge*). This is used for polishing glass. In general, ferrous salts resemble magnesia and manganous salts, with which they are often isomorphous. Those acids whose manganous salts are insoluble in water generally form insoluble ferrous salts; the manganous salts, however, are stable when exposed to the air; the ferrous salts exposed to the air absorb oxygen.

Oxidizing agents change ferrous into ferric salts. Test with MnO_4K, $ClO_3K + HCl$, Br, NO_3H.

What is the general formula of ferric salts? reaction of the soluble salts?

Prepare ferric chloride by adding HCl to a solution of ferrous chloride; then heat gently, and add drop by drop conc. NO_3H until this no longer causes the color of the solution to change. The *oxides* and *hydroxides of the alkali and alkaline earth metals*, as well as almost all those oxides and hydroxides of the heavy metals whose composition is expressed by the formulas MO or $M(OH)_2$, precipitate from cold solutions of ferric salts all iron as ferric hydroxide or basic salt; the *carbonates* of these metals act like the oxides; but with the secondary and primary alkali carbonates the precipitation is incomplete; boiling the mixture, or allowing it to stand for some time, makes the precipitation complete. The precipitate caused by ammonium carbonate is soluble in a large excess of the reagent; when boiled, the precipitation is complete.

Ferric hydroxide is soluble in mineral acids, as is the ferric oxide which has been dehydrated by moderate heat; the highly heated oxide is soluble with difficulty in acids; warmed with conc. HCl or with nearly conc. SO_4H_2 it slowly dissolves; continued boiling with conc. KOH or fusion with SO_4KH renders it soluble in acids. *Oxalic acid* does not precipitate ferric salts.

Alkali acetates color the ferric solution dark red (color of ferric acetate). Boil the very dilute solution; the iron is completely precipitated as basic acetate; the precipitate soon settles and can easily be filtered, if the solution was dilute and if little free acid were present; otherwise it is hard to filter; it must be filtered hot, as, on cooling, the precipitate partially redissolves; test the hot filtered solution for iron. *Disodium phosphate* forms with ferric salts, if they contain no free acid, a yellowish white precipitate (?) easily soluble in mineral acids (?), insoluble in acetic acid. From its solution in acids, therefore, it is precipitated by sodium acetate (?). (Separation of PO_4H_3 from alkaline earths.) Ferric phosphate is partially soluble in an excess of ferric acetate; therefore the precipitation of PO_4H_3 by Fe_2Cl_6 and sodium acetate is incomplete unless the solution be heated to the boiling point (?).

Mix 2 or 3 cc. ferric chloride solution with double the volume of sodium acetate; add one drop of sodium phosphate; the precipitate dissolves on shaking the flask; add 4 or 5 drops of acetic acid, dilute the solution with 15 to 20 times its volume of water, heat to the boiling point, and filter hot; test the filtrate for iron and phosphoric acid; wash the precipitate into a flask, pour $(NH_4)_2S$ over it, let it stand an hour, shaking the

flask from time to time; filter; prove the presence of PO_4H_3 in the filtrate.

Potassium ferrocyanide precipitates from ferric salts Prussian blue (?), soluble in oxalic acid and in ammonium tartrate. How does NaOH act on the precipitate?

Potassium ferricyanide colors the solution brown.

Potassium sulphocyanide colors the solution blood red; the color does not disappear on adding HCl. The presence of much free sulphuric acid, of alkali acetates, tartrates, or citrates weakens or hinders the reaction (very delicate test for iron).

Sulphuretted hydrogen makes ferric solutions milky (?).

Ammonium sulphide forms a black precipitate (?). Ferric salts to which tartaric or citric acid has been added behave like aluminium salts (?); from the alkaline solution all iron is precipitated by H_2S or $(NH_4)_2S$ (?). The precipitation of ferric salts by alkaline hydroxides is also hindered by certain alcohols (glycerin, mannite) and by the sugars. (This fact is utilized in making non-acid ferric solutions as medicines; as *globulis martialis ferr. oxyd. saccharat. solubile.*)

Ferric oxide is a weak base; all its soluble salts, including the basic salts, have acid reaction; it is too weak a base to decompose ammonium salts (?).

The normal ferric salts of the oxygen acids are decomposed by boiling their dilute solutions; basic salts are precipitated (?). Reducing agents change ferric into ferrous salts; test with HCl and Zn (?), or Sn (?), or Fe (?), with H_2S (?), with SO_2 (?), with KI (?).

A dilute solution of ferric chloride and potassium ferricyanide is turned blue by the minutest traces of H_2S or SO_2 (?) (very delicate test for reducing agents).

Iron compounds form with borax a bottle-green bead in the reducing flame; in the oxidizing flame it is brown red to yellow red, when cold colorless.

Fuse some iron compound with soda on charcoal in reducing flame; dissolve the residue in water; a black powder remains, which is attracted by the magnet (?).

How can you recognize ferrous and ferric compounds when both are present? How can you separate them? How can you separate iron from the alkali metals? from the alkaline earth metals? from the earth metals? from manganese? How does iron occur in nature? Name the most important ores (?). For what is iron pyrites utilized? How is iron obtained from its ores?

25. ZINC.

What is the difference between stick zinc, granulated zinc, and zinc dust? When heated, zinc melts, then burns, forming white fumes (?). Exposed to moist air it becomes covered with a layer of basic carbonate (?); dilute HCl or SO_4H_2 dissolves zinc with effervescence (?); the less pure it is, the quicker it dissolves (?); cold dilute NO_3H dissolves it without escape of gas (?), concentrated NO_3H with escape of gases (?). Zinc dissolves in NaOH; when heated, a gas escapes (?); the reaction is hastened by addition of iron filings (?).

Zinc forms only one compound with O. The zinc salts are white and mostly soluble in water; those

insoluble in water are soluble in acids. The soluble salts have an acid reaction and metallic taste. They are poisonous.

Use for the following reactions an aqueous solution of zinc sulphate (white vitriol). Composition and crystalline form (?), solubility in water (?) and alcohol (?). It is used in medicine and in dyeing. *Alkaline hydroxides* form a white precipitate (?) soluble in excess of reagent (?), forming zincates. The concentrated solution remains clear when boiled; if strongly diluted and boiled, most of the zinc is precipitated as $Zn(OH)_2$ (?). From the solution of zincate H_2S precipitates all Zn (?).

Ammonia precipitates Zn salts (?); the least excess of the reagent dissolves the precipitate (?); (difference from Mg). Acid solutions of Zn salts, or those to which NH_4Cl has been added, are not precipitated by ammonia (?). What other metal salts behave in the same way? *Alkaline carbonates* precipitate at the boiling point, and in absence of ammonium salts (?), all zinc as basic carbonate (?), insoluble in excess of the reagent. *Ammonium carbonate* forms the same precipitate, soluble in excess of the reagent (?).

Add Na_2CO_3 to a boiling solution of $ZnSO_4$; filter; wash the precipitate thoroughly with hot water; dry it and ignite it (?). Zinc oxide (zinc white used as paint) is insoluble in water, soluble in acids; when heated turns yellow, on cooling white.

Sulphuretted hydrogen does not precipitate zinc salts if free mineral acid be present (?), but from solutions containing the zinc as citrate, acetate, sulphocyanide, H_2S precipitates all zinc (?). ZnS is insoluble in alkaline hydroxides or sulphides, in acetic, citric, or sulphocyanic acid, soluble in mineral acids. Neutral zinc salts are partially precipitated by H_2S (?); $(NH_4)_2S$ precipitates all zinc as ZnS (?); the precipitation is hastened by addition of NH_4Cl, as is the case with all sulphides of the ammonium sulphide group.

Potassium ferrocyanide forms a white precipitate insoluble in dilute HCl (?).

All zinc compounds heated alone, or with soda, form on the charcoal a coating, yellow while hot, white when cooled, *without* metallic bead (?). ZnO and many other zinc compounds heated on charcoal after moistening with cobalt nitrate, form a green mass (?) (green vermilion paint); *very characteristic* reaction. How can you separate zinc compounds from those of the metals already treated? What are the most important zinc ores? How is zinc obtained from its ores? How is it utilized in the laboratory? What are the principal impurities in commercial zinc? How can these be removed?

26. COBALT AND NICKEL.

Cobalt and nickel are silver-white metals, fusible with difficulty. They are attracted by the magnet, are slowly soluble in dilute non-oxidizing acids (?), easily soluble in nitric acid (?).

Both metals form several oxygen compounds, of which the cobaltous and nickelous oxides (?) have basic character (?) and form stable salts.

Cobalt and *nickel salts*, also called *cobaltous* and *nickelous salts.*

Cobaltous salts with water of crystallization, and in solution, are red, when dehydrated they are blue. Add conc. HCl in excess to the solution of cobalt salt; it becomes blue (?); only cobalt sulphate is red, both with water and dehydrated. The nickel salts with water of crystallization, or in solution, are green, when dehydrated yellow. Test the reaction of the aqueous solutions (?); when ignited the salts are decomposed, excepting the sulphates, which are very stable and require a very high heat for decomposition. Use for the following reactions solutions of the nitrates. How is cobalt nitrate utilized as blowpipe reagent?

Alkaline hydroxides precipitate from solutions of nickel salt a bright green stable precipitate (?); from cobalt solutions, first, blue basic salt; on further addition of the reagent, and gentle heat, red hydroxide (?), which quickly loses its color, and on continued boiling becomes brown (?). Both hydroxides are insoluble in excess of the reagent; easily soluble in acids. (Prepare these precipitates, wash them, and preserve them for use later on.) Heat nickel hydroxide sharply; you obtain NiO. The same treatment of $Co(OH)_2$ yields brown CoO, but the CoO must be cooled in an indifferent gas (?).

Ammonia forms with nickel salts a greenish precipitate (?). An excess of ammonia dissolves it with blue color (?). Cobalt salts yield with ammonia a precipitate of blue basic salt (?), which dissolves in excess of NH_3 to a reddish solution (?); this soon turns brown (?).

If the solution of the nickel or cobalt salts be acid, or if it contain ammonium salt, ammonia does not precipitate it (?).

Alkaline carbonates precipitate from nickel salt solutions pale green, from cobalt salts violet-red basic carbonates (?), insoluble in excess of reagent, easily soluble in ammonium carbonate (?). H_2S precipitates from aqueous solutions of nickel or cobalt salts a little black precipitate (?). If the solutions contain free mineral acid, H_2S causes no precipitate (?). From the warm solution of the acetates, if not too much free acid be present, H_2S precipitates all Ni or Co (?), but precipitates *neither* from the *cold* solution of the citrates, or from the warm solution of the sulphocyanates (?) (separation from Zn).

$(NH_4)_2S$ forms a black precipitate with Ni or Co salts (?). Both sulphides are soluble with great difficulty in dilute HCl (four or five per cent HCl) and in acetic acid; [important for separation from metals described (?)]; in nitric acid or in aqua regia easily soluble; while CoS is insoluble in an excess of $(NH_4)_2S$. NiS is slightly soluble with brown color (characteristic for nickel), and may be reprecipitated from this solution by boiling with acetic acid. *Cobalt peroxide* or *cobaltic oxide*, and *nickel peroxide* or *nickelic oxide*, are very weak bases (?). Their hydroxides are obtained as brownish black precipitates by treating cobalt and nickel salts with energetic oxidizing agents (?) in presence of alkali hydroxide (?). How do the precipitates behave toward hydrochloric acid?

Potassium nitrite [it is better to employ a mixture of concentrated solutions of sodium nitrite and potas-

sium chloride (?)] precipitates from cobalt salt solutions, in presence of an excess of free acetic acid or of dilute nitric acid, on gentle heating, all cobalt as *cobaltic potassium nitrite*, a double salt of potassium nitrite and cobaltic nitrite, $Co(NO_2)_3 + 3NO_2K$ (?); at the same time nitric oxide escapes as gas (?). In concentrated solutions of cobalt salts the precipitate separates at once; from dilute solutions slowly. It is soluble with difficulty in cold water; insoluble in 80 per cent alcohol and in solutions of potassium acetate or chloride; soluble in hot concentrated nitric acid and in hydrochloric acid (?).

In solutions of nickel salts no precipitate is formed by KNO_2 under these conditions unless the solution is very concentrated, when a brownish red precipitate of nickelous potassium nitrite $[Ni(NO_2)_2 + 4NO_2K]$ is formed. If, however, barium, calcium, or strontium salts are present, on adding NO_2K to dilute solutions of Ni salts a yellow precipitate separates; a triple salt, $(NO_2)_6NiK_2M$ (?), supposing M to represent Ba, Sr, or Ca. These salts are soluble with difficulty in cold water, easily soluble in hot water, at the same time decomposing.

Potassium cyanide forms in nickel salt solutions [use a solution of $Ni(OH)_2$ in HCl neutralized as nearly as possible with Na_2CO_3] a greenish white precipitate (?), easily soluble in excess of KCN (?). The precipitate may be separated unchanged from this solution by adding dilute HCl or SO_4H_2, *even* when the solution has been *boiled* some time (?). Add to the solution in KCN an excess of NaOH, heat gently, and add bromine water; all nickel separates as brownish black precipitate (?). If but little nickel be present, the color of the solution becomes inky black (?).

Potassium cyanide forms in cobalt salt solutions [use a solution of $Co(OH)_2$ in HCl, neutralizing excess of HCl with Na_2CO_3] a brown precipitate (?), easily soluble in excess of KCN (?). If to this solution dilute HCl or SO_4H_2 be added *at once*, the precipitate separates again (?), but if the solution be allowed to stand ten minutes, or if two or three drops of dilute HCl be added and the solution *boiled*, dilute acids will no longer precipitate it, as it now contains the cobalt in the form of potassium cobaltic cyanide (?) [in composition analogous to potassium ferricyanide (?)]. This is a very stable compound.

In this solution bromine water with NaOH forms no precipitate; why?

Cobaltoso-cobaltic oxide or *cobaltic cobaltous oxide* (Co_3O_4) is formed when cobalt salts or the hydroxide are moderately heated; exposed to the air it is a black powder. Frequently, in quantitative determinations of CO, it is weighed in this form. The corresponding Ni compound is unstable (?).

Co and Ni compounds fused with soda on charcoal yield a magnetic metallic powder.

The bead of microcosmic salt in both oxidizing and reducing flame is colored deep blue by cobalt compounds; by nickel compounds it is in the oxidizing flame, hot, reddish brown; when cold, pale yellow; in the reducing flame the bead becomes gray (?).

In what forms do Co and Ni occur in nature? Nickel

alloys? How can you separate nickel and cobalt from the metals already described? What marked chemical difference is there between the compounds of Ni and Co and those of Fe?

SEPARATION OF COBALT AND NICKEL.

Method I. founded on the different behavior of the cyanides of cobalt and nickel (?).

Method II. founded on the different behavior of cobalt and nickel salts toward NO_2Na in presence of free acetic acid (?).

Method III. founded on the decomposition of nickel potassium cyanide by yellow oxide of mercury. Precipitate the warm solution of Co and Ni salt with a slight excess (?) of NaOH, filter and wash the precipitate (?), and dissolve it *at once* in hot KCN solution; boil for a few moments (?), add yellow oxide of mercury shaken up with water to the consistency of cream. What happens? Filter, wash, and ignite the precipitate (?) Neutralize the filtrate (what does it contain?) carefully with nitric acid, and add a neutral solution of mercurous nitrate (?) Filter and wash the precipitate formed, and ignite it under the hood (?) What is the residue?

27. SILVER.

White, very malleable metal; insoluble in hydrochloric acid, soluble in hot concentrated sulphuric acid (?) and in moderately conc. NO_3H without heating (?). Silver melts at about 1000°. What are its most important alloys? The silver salts are mostly colorless, sensitive to light (therefore used in photography).

The most important silver salt is the nitrate (?) (lunar caustic). How is it used medicinally? It is a powerful cauterizing agent, forming with albumen insoluble compounds. What is its solubility in water and in alcohol? Reaction of the aqueous solution (?). $AgNO_3$ melts at 200° without decomposing, and on cooling forms a fibrous crystalline mass; high heat decomposes it (?).

Use for the following reactions a solution of silver nitrate. Prepare it as follows: dissolve a silver coin (a ten cent piece will give nitrate enough for these tests) in nitric acid. If the solution is not perfectly clear, dilute and filter it; add HCl as long as a precipitate is formed; filter and wash with water until the wash water no longer has an acid reaction; bring the AgCl into a porcelain dish, stir it with water, and add NaOH; heat to boiling; now add grape sugar in small pieces; this reduces the AgCl to Ag; to reduce the silver chloride obtained from a ten cent piece, five minutes boiling and a piece of sugar as large as a hazel nut should suffice; pour off the liquid; decant a dozen times with water until the water shows no alkaline reaction. Dissolve in a little warm dilute nitric acid, filter in case the solution is not clear, evaporate to dryness on the water-bath; dissolve the crystalline residue in distilled water.

Alkaline hydroxides form in the solution of $AgNO_3$ a brown precipitate of silver oxide (?), insoluble in excess of alkali, easily soluble in dilute NO_3H. How does Ag_2O behave when heated? Ammonia forms the same precipitate, soluble in the least excess of NH_3 (?). If the silver salt solution contains free acid,

ammonia does not form a precipitate (?). *Alkaline carbonates* precipitate yellowish white silver carbonate, easily soluble in NH_3 and in NO_3H (?).

Hydrochloric acid and *chlorides* precipitate AgCl; when shaken and warmed it clots together so that the supernatant liquor is perfectly clear. Test the behavior of AgCl with NO_3H, conc. HCl, NH_3, $S_2O_3Na_2$, and KCN; test the behavior of the solution of AgCl in NH_3 toward an excess of NO_3H. AgCl melts easily, and on cooling forms a horny mass.

Potassium bromide and *iodide* also form precipitates with $AgNO_3$. What is their appearance and their solubility in H_2O, NO_3H, NH_3, $S_2O_3Na_2$, and KCN?

Prussic acid or *potassium cyanide* forms a white precipitate (?), easily soluble in excess of KCN (?) and in NH_3, insoluble in water or dilute acids. *Soluble sulphocyanides* form a white precipitate (?), insoluble in water and dilute NO_3H, soluble in NH_3. *Sodium phosphate* forms a yellow precipitate (?); reaction of the supernatant liquid (?); solubility of the precipitate in NH_3 (?) and in NO_3H (?). K_2CrO_4 forms a brownish red precipitate (?), soluble in nitric acid and ammonia, decomposed by NaOH (?). H_2S forms a black precipitate (?), insoluble in dilute acids, ammonia, and dilute alkaline sulphides, soluble in NO_3H and in KCN (?).

Silver compounds fused on charcoal with soda yield a malleable bead of Ag. Copper, iron, zinc, and many organic substances separate the silver as metal from solutions of silver salts.

In what forms is silver found as ore? How is silver separated from the metals already studied?

28. LEAD.

Soft, ductile metal, easily soluble in NO_3H, scarcely attacked by SO_4H_2 or HCl (?). Lead melts at 326°, and burns when highly heated (?). It forms several compounds with oxygen, of which lead oxide, PbO, and lead peroxide, PbO_2, are the most important. From PbO are derived the lead salts, most of which are colorless and insoluble in water; the soluble salts show an acid reaction with litmus, have a sweetish astringent taste, and are poisonous. Make a solution of lead nitrate for the following experiments.

Alkaline hydroxides precipitate white lead hydroxide, soluble in a great excess of alkali, forming plumbites (?). $Pb(OH)_2$ is but little soluble in water. Those lead salts which are insoluble in water are soluble in excess of alkali (?), for example $PbSO_4$, $PbCO_3$.

Ammonia precipitates a mixture of lead hydroxide and basic salt, insoluble in excess of NH_3; filter and wash the precipitate with water, dry it, and ignite it in a porcelain crucible. The lead oxide thus obtained is a yellow amorphous powder (massicot), which melts when highly heated; on cooling it crystallizes in reddish yellow scales (litharge). Lead oxide is easily soluble in nitric or acetic acid or in hot alkaline hydroxide (?). *Sulphuretted hydrogen* precipitates from neutral, acid, or alkaline solutions, black lead sulphide, insoluble in alkaline sulphides (?), decomposed by hot NO_3H (?). All salts of lead, even the insoluble salts, are changed to lead sulphide by continued treatment with H_2S or $(NH_4)_2S$. Dilute SO_4H_2

or *soluble sulphates* form a white precipitate, but slightly soluble in water, insoluble in alcohol. Lead sulphate dissolves without heating in basic ammonium tartrate or acetate (?), by mixing equal volumes of ammonia and acetic or tartaric acid. It dissolves in sodium hydroxide when heated (?), (separation from SO_4Ba in testing white paint). How can you prove the presence of lead and separate it in the alkaline solution?

HCl or *soluble chlorides* precipitate white $PbCl_2$, nearly insoluble in dilute HCl, soluble with difficulty in cold water, easily soluble in hot water or conc. HCl. $PbCl_2$ is insoluble in ammonia, as basic chloride is formed (?). KI forms a yellow precipitate, soluble in boiling acetic acid; on cooling it crystallizes in golden yellow scales. PbI_2 is also soluble in hot ammonium chloride. *Alkaline carbonates* precipitate basic lead carbonate (?). The precipitate is soluble in alkali and in nitric acid (?). What is *white lead*, and how is it manufactured?

Sodium phosphate precipitates white lead phosphate (?), soluble in NO_3H and in NaOH (?), insoluble in acetic acid. "Sugar of lead" (lead acetate) and "lead vinegar," a basic lead acetate, are important lead salts; what are they and how are they manufactured? Lead chromates have been treated in the chapter "Potassium dichromate."

What is the composition of minium (red lead), and how is it made? How does it behave with HCl? with NO_3H? How is lead peroxide (dioxide) made? Behavior with HCl and with NO_3H? How are the peroxide and minium employed in analysis?

Fused with soda on charcoal, all lead compounds yield a malleable lead bead and yellow coating (?). How can lead compounds be separated from those of the metals thus far considered? What are the most important lead ores? What is the danger in the use of lead pipes for drinking water?

How can the presence of traces of lead in water be detected?

29. MERCURY.

Mercury is the only metal which is liquid at ordinary temperature. It is insoluble in HCl, soluble in hot conc. SO_4H_2 (?), in aqua regia (?). In cold dilute NO_3H in presence of an excess of mercury, part of the Hg dissolves, forming mercurous nitrate (?). In an excess of hot concentrated NO_3H, Hg dissolves, forming mercuric nitrate (?). Metallic mercury, especially when vaporized, and the soluble salts are active poisons. Hg forms two oxides, mercurous oxide, Hg_2O, and mercuric oxide, HgO; both are basic in character (?).

Mercurous salts. Some of these are soluble in water with acid reaction, some are insoluble in water; when much water is added to the solution of the soluble salts, basic salts are precipitated (?).

For the following tests use a solution of mercurous nitrate. *Alkaline hydroxides* form a black precipitate(?). On exposure to light or when heated this decomposes (?). It is insoluble in excess of alkali. NH_3 forms a black precipitate (?). HCl and soluble chlorides precipitate mercurous salts, even in very dilute solution; the white precipitate (calomel) is insoluble in

water and dilute acids, soluble in aqua regia, nitric acid, and in conc. HCl, but is decomposed in solution. Pour NH_3 on calomel; it turns black (?). *Stannous chloride* first forms a white precipitate (?); an excess of the reagent turns it gray (?). KI forms a yellowish green precipitate (?), decomposed by light (?). It decomposes quickly in an excess of KI (?). $K_2Cr_2O_7$ forms a dark red precipitate (?). Test its behavior when ignited (?).

H_2S or $(NH_4)_2S$ forms a black precipitate, which is a mixture of mercuric sulphide, HgS, and finely divided mercury (?), insoluble in $(NH_4)_2S$, soluble in aqua regia (?). If the precipitate be treated with conc. NO_3H a white compound is formed $[Hg(NO_3)_2\ 2HgS]$, soluble in aqua regia. Oxidizing agents (?) convert mercurous salts easily into mercuric salts.

Mercuric salts. Most mercuric salts are insoluble in water, because they have a tendency to form basic salts; the chief exceptions to this rule are the chloride and the cyanide. The chloride is the most important mercuric salt (corrosive sublimate). Test its solubility in water and in alcohol (?). It melts and distills without decomposition. If its aqueous solution or the solution of other mercuric salts in presence of HCl be evaporated to dryness, a part of the mercuric chloride escapes with the water vapor; this volatility can be prevented by adding alkaline chlorides (?).

Use mercuric chloride for the following reactions. *Alkaline hydroxides* form an orange-yellow precipitate, insoluble in excess of alkali (?). If too little alkali is added, a brown precipitate is formed (?). How does the yellow precipitate behave when heated? What is its solubility in water and in acids? How is red oxide of mercury prepared? How is "suspended" mercuric oxide used in analysis?

Ammonia forms a white precipitate (?).

KI forms a vermilion red precipitate (?), insoluble in water, soluble in alcohol and in excess of KI.

Secondary alkaline carbonates form a red-brown precipitate (?); *pure* (free from secondary) *primary alkaline carbonates* form *no* precipitate, but after standing some time a small quantity of a red precipitate is formed (?). (This reaction is of value in testing the purity of primary alkaline carbonates.)

In a solution of mercuric nitrate, both primary and secondary alkaline carbonates precipitate basic carbonate (?). Little H_2S or $(NH_4)_2S$ forms a white precipitate (?); more reagent turns it black (?). The black precipitate is insoluble in nitric acid. In this it differs from the sulphides of all the metals already studied. The precipitate is soluble in aqua regia (?), and in K_2S, if this contains KOH or CO_3K_2. Reducing agents change mercuric salts into mercurous salts or mercury.

A little *stannous chloride* forms a white precipitate; an excess of $SnCl_2$ turns it gray (?). Phosphorous acid precipitates slowly, but fully, all Hg as HgCl (?), but if the temperature be raised the precipitate is mixed with metallic mercury. Mercuric cyanide forms colorless crystals, soluble in water, insoluble in absolute alcohol. $Hg(CN)_2$ is the only cyanide of the heavy metals which is soluble in water. Alkaline hydroxides do not decompose the solution (?). H_2S does (?).

How can mercurous salts be detected in presence of mercuric salts? How can you distinguish and how can you separate HgCl from $PbCl_2$ or AgCl?

All mercury compounds are volatilized when heated, and most of them are decomposed by heat (?). But few (HgCl, $HgCl_2$) are volatile undecomposed.

Metallic mercury separates and is volatilized from all Hg compounds when they are heated with soda (?). Bring a mixture of dry $HgCl_2$ with fused soda (?) into a *dry* glass tube closed at one end, and heat. The volatilized Hg is deposited in the cooler part of the tube as a mirror or in drops (?). In what form is Hg found? How is it prepared? How can you best separate compounds of mercury from those of the metals already studied?

30. BISMUTH.

Reddish white, very brittle metal, fuses at 264°, is insoluble in hydrochloric acid, soluble in NO_3H (?), in aqua regia (?), and in hot conc. SO_4H_2 (?). What are the principal alloys of bismuth? The most important oxygen compound of Bi, bismuth oxide (?), is made by heating the nitrate (try this), or by heating the metal exposed to the air, and forms a yellow powder, insoluble in water and in alkaline hydroxide. Most of the salts corresponding to this oxide are white, and are decomposed by ignition (?). The soluble salts may be dissolved in little water; more water decomposes them, precipitating basic salt, whilst the acid thus set free holds part of the Bi in solution as acid salt (?);

but from the *neutral* solution of the chloride, by adding much water all bismuth is precipitated as basic salt (?). All Bi may be precipitated from the neutral solution of the nitrate by much water and adding dilute sodium chloride solution (?). The basic Bi salts are insoluble in tartaric acid or potassium monotartrate (difference from basic antimony salts). Prepare basic bismuth nitrate; composition (?). It is largely used as cosmetic and in medicine. *Alkali hydroxides* and NH_3 form in Bi salt solutions a white precipitate (?), insoluble in excess of the reagent. If the precipitation is made in the boiling liquid, or if the precipitate from the cold liquid be dried at 100°, the hydroxide BiOOH, is formed (?). *Alkaline carbonates* precipitate at the boiling point all Bi as basic carbonates (?), almost insoluble in excess of the reagent. Behavior of the precipitate when ignited (?).

H_2S precipitates from not too acid solutions and from neutral or alkaline solutions all Bi as sulphide (?), soluble in hot conc. HCl (?) or in NO_3H (?).

Add NaOH to a solution of *stannous chloride* until the white precipitate (?) first formed has dissolved and more NaOH no longer forms a precipitate; now add gradually to this solution a solution containing a Bi compound; a black precipitate of bismuth suboxide, BiO, is formed. This is a delicate test for Bi compounds.

$$[4Bi(OH)_3 + Sn_2O_2Na_2 + 2NaOH = 2SnO_3Na_2 + 4BiO + 7H_2O].$$

All compounds of Bi heated on charcoal with soda yield a brittle metal button and a dark yellow coating (?).

How does bismuth occur in nature? How can you separate Bi compounds from those of the metals already considered?

31. COPPER.

Red, ductile metal, requires great heat to fuse it; a green coating forms on it when exposed to moist air for a long time (?); when heated exposed to the air it is changed to black oxide (?). Copper is soluble in hot conc. SO_4H_2 (?), in cold dilute NO_3H (?), in aqua regia (?). How is chemically pure copper obtained? Use of copper in alloys (?) Brass (?) Bronze (?) Copper and nickel coins (?).

Copper forms two important compounds with oxygen, cuprous oxide, Cu_2O, and cupric oxide, CuO; both have basic character (?).

Cuprous oxide: If cupric salts are heated with grape sugar, or arsenious acid, in presence of an excess of NaOH, yellow cuprous hydroxide is formed (?), which on heating more strongly is changed into red Cu_2O.

Cupric oxide: How is it made? solubility in acids? How is CuO used as an oxidizer? What is the principle of the analysis of carbon compounds by combustion? The salts corresponding to this oxide are in solution, or with water of crystallization, blue or green; anhydrous, they are mostly white. Use for the following reactions a solution of cupric sulphate (blue vitriol); how is it made? what is its composition? solubility? behavior when heated? NaOH forms a bluish precipitate in cold solutions (?); on boiling it becomes black, and is insoluble in excess of the reagent. In presence of tartaric or citric acid, of glycerin and other organic compounds, *alkaline hydroxides* form no precipitate in solutions of cupric salts (Fehling's solution for determination of glucose). *Ammonia* first forms a greenish (?), then a bluish precipitate (?), which dissolves in excess of NH_3, forming a dark blue liquid (?). In a thick layer of the liquid this color is perceptible in a dilution of 1 part of copper in 100,000 of water. (Delicate test for copper compounds.) *Ammonium carbonate* acts like NH_3.

Alkaline carbonates form in the cold solution a blue precipitate of basic carbonate (?), which, on standing, or when washed with cold water, turns green (?).

$Fe(CN)_6K_4$ forms a reddish brown precipitate (?), insoluble in dilute acids, decomposed by NaOH (?) or by strong acids. If only traces of copper are present in a solution, $Fe(CN)_6K_4$ imparts a reddish color to the solution. (This is the *most delicate* test known for copper compounds.) KI precipitates *cuprous iodide* and iodine (?), but if sulphurous acid be added to the solution, a pure white precipitate is formed (?), insoluble in water and dilute acids, soluble in $S_2O_3Na_2$ or in NH_3. *Soluble cyanides* form a reddish precipitate (?) which soon turns green (?); when warmed it turns white (?); this reaction is hastened when sulphurous acid is added. The precipitate is easily soluble in an excess of KCN (?). From this solution H_2S does *not* precipitate copper (difference from cadmium salts).

Soluble sulpho-cyanides form in concentrated cupric salt solutions a black precipitate (?), which when

warmed, or on an addition of sulphurous acid, turns white (?). The white compound is insoluble in water and dilute acids. (Important for the volumetric determination of copper compounds.) H_2S and $(NH_4)_2S$ form a black precipitate, insoluble in dilute acids or in K_2S, partially soluble in yellow $(NH_4)_2S$ (?), easily soluble in NO_3H (?) or KCN (?). The precipitate is oxidized by exposure to the air (?). When ignited in a current of hydrogen, cupric sulphide is reduced to cuprous sulphide. Iron and zinc precipitate metallic copper (?). Test this in a platinum dish with a solution of $CuSO_4$ to which 4–5 drops of HCl and a fragment of zinc have been added.

All copper compounds when heated with soda on charcoal yield red metallic scales; these can be best seen by powdering the fused mass with water in a porcelain mortar and pouring off the water.

Add copper salt to the borax or microcosmic salt bead; the oxidizing flame colors it greenish blue (?), the reducing flame causes it to appear (after cooling) opaque and red (?). By this last reaction the copper bead can be distinguished from another similarly colored bead (?).

In what forms does copper occur in nature? How is it obtained from its ores? How can you separate copper compounds from those of the metals already studied? and how can you recognize its presence in a solution of different metallic salts, without separation?

32. CADMIUM.

White, very ductile metal; melts at 315°, and burns when heated, with brown vapor (?). In dilute HCl or SO_4H_2 slowly soluble, in NO_3H easily soluble. Cadmium forms only an oxide, CdO; the salts are mostly colorless; those which are insoluble in water are soluble in acids. Aqueous solutions of Cd salts turn blue litmus red and have a metallic taste. Use a solution of $CdSO_4$ for the following reactions. NaOH forms a white precipitate (?), insoluble in excess of reagent; filter, wash, and ignite the precipitate; what is the residue? test its solubility in water and acids.

NH_3 forms the same precipitate, easily soluble in excess of the reagent (?). *Alkaline carbonates* precipitate white $CdCO_3$, insoluble in excess of the reagent.

H_2S and $(NH_4)_2S$ precipitate yellow sulphide, insoluble in dilute acids, or in alkaline hydroxides, or sulphides, or in KCN. Nitric acid, conc. HCl and boiling SO_4H_2 (1 part acid, 6 parts water) dissolve the sulphide readily (?). KCN forms a white precipitate (?), easily soluble in excess of KCN (?). From this solution H_2S precipitates *all* Cd (difference from Cu).

Cadmium compounds fused with soda on charcoal form a brown coating (?), but no metal button.

In what forms is Cd found in nature? What other metal does Cd strongly resemble in many respects? How can you separate cadmium compounds from those of the metals already described?

33. ANTIMONY.

Very brittle metal, fuses easily, burns when heated, with white inodorous vapor and blue flame (?); insoluble in HCl, easily soluble in aqua regia (?). NO_3H oxidizes it, according to the concentration of the acid, to antimony oxide (?), or to metantimonic acid (?), or to a mixture of both (?). Sb forms two compounds with O; antimony oxide, Sb_2O_3 (antimonious anhydride), and antimony pentoxide, Sb_2O_5 (antimonic anhydride); the former has weak basic character, the latter chiefly the properties of an anhydride.

To what natural group of elements does Sb belong?

Antimony oxide, formed by burning antimony (?), is white, almost insoluble in water or NO_3H, soluble in HCl or tartaric acid (?). Use a solution of Sb_2O_3 in HCl for the following reactions. A hydroxide, SbO.OH, corresponding to the oxide, is precipitated from Sb salt solutions, by NaOH, NH_3, or alkaline carbonates (?). This hydroxide is also called metantimonious acid, and dissolves in an excess of NaOH, forming sodium metantimonite (?). The antimony salts are derived either from the normal hydroxide $Sb(OH)_3$, for example $SbCl_3$, or from the hydroxide SbO.OH; in the latter case the univalent group $\overset{III}{Sb}=O$ (antimonyl) replaces one hydrogen atom of the acid, i. e. it acts as a univalent metal; thus the basic antimony salts (or antimonyl salts) are formed; for example, $(\overset{III}{Sb}=O)Cl$.

An important salt is antimonyl potassium tartrate (tartar emetic); composition (?), and solubility in water (?). With exception of the tartrate, the antimony salts are unstable. Those which are soluble in water are decomposed by much water; antimonyl salts are precipitated, and the acid thus set free holds part of the Sb in solution as acid salt. For example, the solution of $SbCl_3$ in little water is decomposed by more water, forming basic antimony chlorides of varying composition (according to the amount of water). What is "powder of algaroth"? An excess of HCl dissolves these precipitates (?). The presence of tartaric acid, or monopotassium tartrate, prevents the decomposition of the antimony salts by water (?); (difference from bismuth salts). Try all these reactions. H_2S forms in the acidulated solution of antimony salts an orange-red precipitate (?). This is insoluble in dilute acids, but little soluble in NH_3 or ammonium carbonate, soluble in concentrated warm HCl (?) or in aqua regia (?). Antimony trisulphide is soluble in alkaline hydroxides, forming metantimonite and sulphantimonite (?); in alkaline sulphides forming sulphantimonite (?); in alkaline polysulphides, forming sulphantimoniate (?). What is precipitated from these solutions by adding dilute SO_4H_2 or HCl? What are sulpho salts?

Add NaOH to the solution of an antimony salt until the precipitate formed is redissolved (?); add to this solution NO_3Ag, and then add NH_3; a black precipitate is formed (perhaps silver suboxide, Ag_4O; perhaps a mixture of Ag and Ag_2O; the composition is not fully determined), while the antimonite is oxidized to antimoniate (?); (difference from antimonic acid).

Antimonic acids: Two antimonic acids are comparatively well known, metantimonic acid (?) and pyro-antimonic acid (?), corresponding in composition to the phosphoric acids of like names. Both acids gently heated yield antimonic anhydride (?). The first acid is formed by the action of hot conc. NO_3H on Sb (?), the second by mixing $SbCl_5$ with water (?); both acids are almost insoluble in water or nitric acid, but are soluble in conc. HCl (?), in tartaric acid, or in KOH (?). Most metantimoniates are soluble with difficulty or insoluble in water. The alkaline pyro-antimoniates are formed when metantimonic acid or its alkaline salts are fused with a large excess of alkali hydroxide, in a silver or Hessian crucible (?). Potassium pyro-antimoniate is decomposed by water into KOH and secondary potassium pyro-antimoniate, which dissolves in water at 40°–50°, and is used as reagent for sodium salts. If this solution is added to a not too dilute neutral sodium salt solution, a white crystalline precipitate is formed, $Sb_2O_7Na_2H_2+6H_2O$, which is soluble with difficulty in water, and nearly insoluble in alcohol. (Important for the separation of Sb from Sn and As.)

Use for the following reactions a solution of metantimonic acid in HCl (?); H_2S forms in the cold (not too acid) solution an orange-red precipitate (?) (gold sulphur). Behavior toward conc. HCl (?), aqua regia (?), alkaline hydroxides (?), ammonia (?), alkaline sulphides (?), ammonium carbonate (?), nitric acid (?).

What is the composition of "Schlippe's salt," and how is it prepared? If the antimonic acids, or antimony pentachloride, be warmed with HCl and *pure* (?) KI, the liquid turns brown, and contains then free iodine (?); [important reaction for antimonic acid (?)]. How would antimony oxide thus treated behave?

Reactions common to *antimonious* and *antimonic* compounds: 1. Bring a solution containing Sb (oxidizing acids must not be present) into a platinum dish (or into a porcelain dish with a piece of bright platinum foil); add a piece of zinc and dilute HCl; a little hydrogen antimonide gas (stibine) escapes, and metallic Sb is deposited as brown or black coating on the platinum (?). Pour off the liquid, wash with water, and touch with a stirring-rod moistened with NO_3H. By contact with the NO_3H the Sb is oxidized (?); (delicate reaction; difference between Sb and Sn or As compounds).

2. Fused with soda on charcoal in the reducing flame, all Sb compounds yield a brittle metallic button; heated in the oxidizing flame, the metal is volatilized as inodorous white vapor (?), at the same time the charcoal is coated white (?).

How can you recognize antimonious compounds and antimonic compounds, when both are present? What are the most important alloys of Sb?

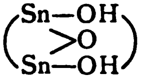
In what forms is Sb found in nature? How can you separate Sb compounds from those of the metals studied?

[One important Sb compound, hydrogen antimonide (stibine), will be considered together with the corresponding compound of arsenic.]

34. TIN.

White, soft, ductile, stable when exposed to dry or moist air; it melts at 229°, and burns at white heat in contact with air. What is formed when it burns? What are the principal impurities in commercial tin? Tin is soluble in hot conc. HCl (?), in aqua regia (?), and in conc. SO_4H_2 (?). Very dilute cold nitric acid changes Sn into stannous nitrate without escape of gas (?). Conc. hot nitric acid changes the Sn into meta-stannic acid (?). What are the important alloys of tin? To what group of elements does it belong? Tin forms two oxygen compounds, stannous oxide, SnO, with basic properties, and stannic oxide (stannic anhydride), SnO_2, with mainly acid properties.

Stannous salts: These are colorless; their solutions are oxidized by the air (?). Those insoluble in H_2O are soluble in HCl. The most important stannous salt is the chloride ("tin salt"). How is it made? How is it employed in analysis? Use for the following reactions a freshly prepared solution of stannous chloride. ***Alkaline hydroxides, ammonia, ammonium carbonate***, precipitate white stannous hydroxide, $Sn_2O_3H_2$



$\left(\begin{array}{l} Sn-OH \\ \quad >O \\ Sn-OH \end{array}\right)$; soluble in excess of alkali, forming stannites (?); boil the solution; it decomposes (?). How is the stannite used as reducing agent?

H_2S forms in the not too acid stannous salt solution a brown precipitate (?), insoluble in dilute acids and Na_2CO_3, nearly insoluble in colorless (?) alkaline sulphide, soluble in strong HCl (?), in aqua regia (?), and in alkaline polysulphides (?), forming sulpho-stannates. In the sulpho-stannate solution dilute acids form a yellow precipitate (?). How does SnS behave when treated with NO_3H?

Stannous salts are powerful reducing agents; try the action of $SnCl_2$ on mercuric and ferric salts, and on $Cr_2O_7K_2$ (difference from stannic salts).

Stannic compounds: Stannic oxide, or stannic anhydride (how is it prepared?), is a white powder which becomes dark yellow when heated; high heat renders it insoluble in water, acids, or alkaline hydroxides. It may in this case be changed into a soluble compound by fusion with NaOH in a silver crucible (?).

Two modifications of the hydroxide derived from SnO_2 are known, which are called stannic acid and meta-stannic acid. Both have probably the same composition (SnO_3H_2), but different molecular weight; the molecular weight of meta-stannic acid is the greater.

Stannic acid is the white precipitate formed by adding NaOH to stannic chloride (?). How can you obtain a solution of stannic chloride? What is the substance known commercially as "preparing salts"? Stannic acid is soluble in dilute HCl (?), in SO_4H_2 or NO_3H (?), in NaOH (?).

Meta-stannic acid is formed by oxidizing Sn with NO_3H (?); insoluble in NO_3H or SO_4H_2. When warmed with *conc.* HCl it is changed into white *meta-stannic chloride* (?), which is insoluble in the acid, but soluble in water. When meta-stannic acid is boiled with NaOH, sodium meta-stannate is formed, insoluble in NaOH, but soluble in water (difference from stannic

acid). Fuse meta-stannic acid with NaOH in a silver crucible; the sodium salt of *stannic acid* is formed.

Dilute SO_4H_2 precipitates from the cold solution of *meta-stannic* chloride (even if much free HCl be present) all tin as meta-stannic acid (difference from stannic chloride).

H_2S forms in not too acid stannic salt solutions a yellow precipitate (?), insoluble in dilute acids, soluble in conc. HCl or aqua regia (?), very easily soluble in alkaline hydroxides (?) or sulphides (?), and may be reprecipitated from these solutions by dilute acids. SnS_2 is soluble with difficulty in NH_3, practically insoluble in ammonium carbonate. How does SnS_2 behave with NO_3H?

Reactions common to *stannous* and *stannic compounds:* 1. Bring a soluble compound of tin into a platinum dish with zinc and dilute HCl. Metallic tin separates as a gray spongy mass, or as crystals clinging to the *zinc*, without discoloring the platinum (?).

2. Fused with soda and a little KCN, on charcoal, all tin compounds yield white ductile scales of metal and a very slight white coating on the charcoal (?). How can you distinguish stannous and stannic compounds when both are present in a solution? How can you separate tin from the metals described? How is tin found in nature? How is tin commercially prepared?

35. ARSENIC.

Two modifications of arsenic are known, amorphous arsenic (a black mass), and crystallized arsenic (steel-gray hexagonal rhombohedra). When heated exposed to the air, arsenic burns with a bluish white flame and white vapor, with a peculiar garlic-like odor, forming arsenic trioxide. As is insoluble in HCl or dilute SO_4H_2. NO_3H oxidizes it, according to the concentration of the acid and length of action, to arsenious (?) or arsenic (?) acid. Aqua regia or HCl and $KClO_3$ oxidize it to arsenic acid (?). In what group of elements does As belong? Arsenic forms two oxygen compounds: trioxide, As_2O_3 (white arsenic), and pentoxide, As_2O_5 (arsenic anhydride).

Arsenic trioxide: How is it commercially prepared? It is a powerful poison. What is the best antidote for arsenic? Arsenic oxide is easily sublimed without fusion; solubility in water (?), in HCl (?), in alkaline hydroxides and carbonates (?) (Fowler's solution).

The arsenites of the alkaline metals are derived from a metarsenious acid, AsOOH, which has not been isolated (compare with antimony). Most other arsenites are derived from normal arsenious acid, $As(OH)_3$, which also has not been isolated. Only the arsenites of the alkaline metals are easily soluble in water; the other arsenites are soluble with difficulty, or insoluble in water, but are all soluble in acids. Use for the following reactions a solution made by heating primary alkaline carbonate with an excess of As_2O_3.

Neutral NO_3Ag precipitates yellow AsO_3Ag_3 (?), soluble in NH_3 (?) or NO_3H (?). In order to produce this reaction in an aqueous solution of As_2O_3, add NO_3Ag, and blow NH_3 vapor across the surface of the solution (?).

Cupric sulphate forms a green precipitate, AsO_3HCu (Scheele's green), soluble with blue color in NaOH; from this solution when heated red, cuprous oxide separates (?) (characteristic reaction of As_2O_3). What is Schweinfurt green? Solubility? Why is it dangerous to health? A solution of iodine in KI becomes colorless when AsO_3Na is added (?) (characteristic reaction for As_2O_3. How is this reaction utilized in volumetric analysis?)

H_2S forms, in the solution of As_2O_3 acidulated with HCl, or of arsenites, a lemon-yellow precipitate (?), insoluble even in conc. HCl, soluble in aqua regia (?), nitric acid (?), alkaline hydroxides (?), ammonia (?), ammonium carbonate (?), alkaline sulphides (?) and polysulphides (?). If the solution of As_2S_3 in the last five reagents be mixed with dilute HCl or SO_4H_2, a yellow precipitate again separates (?). H_2S is the best reagent for precipitating As, as the precipitation is complete, even from solutions containing much free HCl.

How can you prepare arsenic trichloride? What are its properties?

Arsenic pentoxide: white glacial mass, soluble in hot water, yielding ortho-arsenic acid (?), which forms a strongly acid solution. In what other way is arsenic acid formed? Arsenic acid is a white deliquescent crystalline mass.

Only the arsenites of the alkaline metals are soluble in water; all others are soluble with difficulty or insoluble in water, but soluble in mineral acids.

Use for the following reactions a solution of arsenic acid neutralized with NaOH.

Neutral NO_3Ag forms a reddish brown precipitate (?), easily soluble in NH_3 or NO_3H (?).

A solution of ***ammonium molybdate*** in nitric acid, added in excess to the solution of arseniate, forms, on gently heating, a yellow precipitate (?) similar to that formed by phosphates under the same conditions; soluble in NH_3, insoluble in NO_3H.

A mixture of ***magnesium sulphate***, NH_4Cl, and NH_3 (so-called ***magnesia mixture***) forms a white crystalline precipitate (?), soluble with difficulty in water, almost insoluble in water containing NH_3. How can you distinguish this salt from the corresponding phosphate? (characteristic reaction for AsO_4H_3, particularly in presence of As_2O_3). H_2S yields in a cold solution of AsO_4H_3, or in an acidulated solution of arseniate, first a precipitate of S. Not until *all* arsenic present is reduced to arsenious acid does H_2S precipitate the As as trisulphide. The quickest way to precipitate the As is first to reduce to arsenious acid by heating the solution with sulphurous acid; drive off the excess of SO_2 by boiling, then precipitate with H_2S; but by conducting H_2S into a solution of arsenic acid which is kept nearly at the boiling point, all As is slowly precipitated as yellow As_2S_5, arsenic pentasulphide. Test the action on the pentasulphide of all the reagents used with the trisulphide (?).

How can you recognize arsenious and arsenic acids when both are present? How can you separate As from the metals previously studied? In what forms does As occur in nature?

GENERAL REACTIONS FOR ARSENIC COMPOUNDS.

1. All As compounds yield when heated with the reducing flame on charcoal alone, or better, mixed with soda and KCN, the characteristic garlic odor; very small quantities of As may thus be recognized.

2. H_2S precipitates from the (with HCl) acidulated solutions of all arsenic compounds, either cold or warm (?), all As as sulphides, soluble in alkaline sulphides and reprecipitated by dilute SO_4H_2.

3. All As compounds mixed with six times the amount of a *dry* mixture of equal parts of Na_2CO_3 and KCN, and fused in a dry glass tube sealed at one end, form on the cold part of the tube a bright mirror of metallic arsenic. Formulate this reaction for As_2O_3 (?), for As_2S_3 (?).

(This test is best made in a tube, the sealed end of which is blown out to a bulb; the bulb should be only half filled with the mixture; if any moisture escapes on first heating, wipe it off with a strip of filter paper.)

4. *Marsh's method:* If compounds of arsenic are brought together with zinc and dilute HCl or SO_4H_2, a mixture of hydrogen and *hydrogen arsenide* (arsine), AsH_3 escapes (?). The latter is a very poisonous gas, of disagreeable odor. Its reactions are so characteristic and delicate that the minutest traces of arsenic can be detected by means of it. If antimony compounds are treated in the same way, inodorous SbH_3 escapes (?), which in many respects resembles the corresponding As compound, but may be easily distinguished from it by several reactions.

Apparatus for Marsh's Method.

The flask should be of 150 to 200 cc. capacity; the funnel tube should reach nearly to the bottom of the flask; the exit tube is connected by pure rubber tubing with a tube containing calcium chloride, and this with the hard glass tube, which should be about 7 mm. in diameter, and is drawn out in two or three places, and the end bent upwards and drawn out. Bring into the flask some pieces of *pure* zinc (?) and *pure* dilute SO_4H_2 (1 part conc. acid, 5 parts water) or dilute HCl. Now wait at least ten minutes to avoid explosion (?), then light the gas at the bent end of the tube. Now pour the solution you wish to test for arsenic, or antimony, through the funnel tube into the flask, and test as described below.

Of course, in this method the solution examined must *not* contain oxidizing agents.

(*Work under the hood.*)

Arsine (*Hydrogen arsenide*).	Stibine (*Hydrogen antimonide*).
The lighted gas burns with —	
Bluish white flame (?) and white vapor (?).	Greenish white flame (?) and white vapor (?).
On a porcelain dish held in the flame a moment, are formed—	
Shining brownish black spots (?):	Black less shining spots (?):
Which, when touched with a conc. alkaline solution of sodium hypochlorite,	
Immediately disappear (?).	Do not disappear.

If the spots are touched with a drop of hot nitric acid—

They disappear (?). Add to the solution a drop of NO_3Ag; hold a stirring-rod moistened with NH_3 over it; the drop is colored either yellow or brownish red (?).	They turn white (?). Treat them with tartaric acid, and conduct H_2S into the solution; an orange red precipitate is formed.

Heat the hard glass tube with the Bunsen flame just BEFORE *one of the places where it is drawn out; a mirror is formed of—*

Metallic arsenic (in thin coating, translucent, with brown color). *Without fusing*, can be driven further on in the tube in a stream of hydrogen, by gentle heat.	Metallic antimony. Can be volatilized with difficulty, and *not* till the metal is first fused.

Conduct through the tube in which the mirror of As *or* Sb *has been formed, a current of* DRY H_2S, *and heat the tube gently where the mirror is formed; they are changed—*

To yellow volatile As_2S_3 (?):	To black or partially orange Sb_2S_3 (?):

Which, when you conduct a slow current of DRY HCl *over it—*

Remains unchanged (?). Conduct AsH_3 into NO_3Ag solution; metallic silver separates (?). Add NH_3 cautiously to the filtrate; yellow silver arsenite is precipitated (?).	Disappears (?). Conduct SbH_3 into NO_3Ag solution, and Sb is precipitated in the form of silver antimonide (?). Heat the precipitate with tartaric acid and water, and the antimony dissolves, and can be precipitated by H_2S (?).

5. Bring a soluble arsenic compound, a fragment of pure zinc, and some dilute sulphuric acid into a test tube; push a stopper of cotton wool into the mouth of the tube; cover the tube with a piece of filter paper, in the middle of which you have put one drop of a solution of one part NO_3Ag in one part water; the

paper turns lemon-yellow, first on the under side, then on the upper side, while on the periphery of the spot a brownish black circle forms which gradually spreads toward the middle and finally blackens the whole spot. The yellow compound has the composition $AsAg_3 3(NO_3Ag)$. Formulate the reaction (?). If you wet the spot (while it is still yellow, with only the black edge) with water, it instantly turns black, in consequence of the formation of metallic silver, $2[AsAg_3 3(NO_3Ag)] + 3H_2O = Ag_{12} + 6NO_3H + As_2O_3$. This reaction is valuable for the purpose of detecting the presence of *very minute traces of* As. In making the above tests you must first convince yourself of the purity of the reagents, and use perfectly clean glassware.

ANALYTICAL TABLES

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I.—PRELIMINARY TESTS.

1. Flame reaction of substance on platinum wire; if the substance is a liquid, evaporate it to dryness.

Yellow.	Violet.	Dark Red.	Red.	Yellowish Green.	Green.
Na	K	Sr*	Ca*	Ba*	Cu BO_3H_3†

Potassium in presence of sodium can be detected by looking through blue glass at the flame, which will, if K is present, appear reddish violet.

2. Microcosmic bead.

Color of Bead	in presence of
Reddish Brown,	Iron oxide, Nickel oxide.
Violet,	Manganese compounds.
Blue,	Cobalt oxide.
Green,	Copper oxide, Chrome oxide.

Silicates yield a skeleton of silica.

3. Mix the powdered substance carefully with sodium carbonate (or the carbonate and potassium cyanide), moisten with water, and heat on charcoal in reducing flame of blowpipe until the mass melts.

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* Particularly after moistening with HCl.

† In salts after moistening with SO_4H_2.

Hepar.	Odor of Garlic.	Metal Beads without Coating.		Metal Beads with Coating.		Coating without Bead.	Explosive Combustion
		Ductile Grains.	Gray Magnetic Powder.	Brittle Metal.	Ductile Metal.		
Sulphur Compounds	Arsenic Compounds	Tin Silver Copper	Iron Cobalt Nickel	Antimony, White c'ting Bismuth, Brown c'ting	Lead, Yellow coating	Cadmium, Brownish red Zinc, White	Nitrates Chlorates Iodates Perchlorates

4. Moisten the substance on the charcoal, or on the platinum wire, with cobalt nitrate, and heat for some moments until the color no longer changes.

Blue Bead.	Blue Infusible Mass.	Gran. Mass.	Pale Red Mass.	Brown Mass.	Gray Mass.
Phosphates Borates Silicates of the Alkali Metals.	Al_2O_3, Phosphates of the Earth Metals, Silicic Acid, Some Silicates.	Zinc Oxide, Yellowish Green. Tin Oxide, Bluish Green. Antimonic Acid, Greenish.	MgO	BaO	CaO SrO

5. Heat the substance on the platinum foil or in a dry test tube. If the substance is entirely or partially volatilized, it may contain ammonium, mercury, or arsenic compounds. If it turns more or less black, organic matter is present. If colorless drops of liquid form on the colder part of the tube, the substance contains water.

II.—SOLUTION.

After making the preceding tests, boil the powdered substance with water. If it does not dissolve entirely,

filter. Evaporate a few drops of the filtrate on the platinum foil to dryness. A residue proves that the substance is partially soluble in water.

Test the reaction of the aqueous solution with litmus paper.

If the substance is partly or quite insoluble in water, try HCl. If a part or all is insoluble in HCl, try NO_3H. (If the preliminary tests indicate lead or silver, use NO_3H at first, instead of HCl.) (Why?)

If a part or all of the substance is insoluble in NO_3H, test it with aqua regia (one part NO_3H and three parts HCl). Always heat the solvent with the substance. If after treatment with aqua regia a residue remains, treat as directed under X.

III.—SOLUBILITY OF THE MORE COMMON COMPOUNDS.

1. *Soluble in water.*

Of the alkalies, K, Na, NH_4:

The hydroxides, the chromates and dichromates, sulphates, phosphates, borates, oxalates, carbonates, chlorine, bromine, iodine and fluorine compounds, sulphides, nitrates, silicates (K and Na silicates), acetates, cyanides, arsenites, arsenates, the ferro- and ferricyanides.

Of the alkaline earths, Ca, Ba, Sr, Mg:

The hydroxides and sulphides of Ba and Sr, magnesium sulphate and chromate, the chlorides, bromides, iodides, nitrates and acetates of all.

Of the earths, Al and Cr:

The chlorides, bromides, iodides, nitrates, acetates, sulphates and tartrates (anhydrous $CrCl_3$ and $CrBr_3$ are nearly insoluble in both water and acids).

Of the heavy metals of the ammonium sulphide group, Mn, Zn, Ni, Co, Fe:

Sulphates, chlorides, bromides, nitrates, acetates.

Of the metals of the hydrogen sulphide group:

1st Class: Ag, Pb, Hg, Cu, Bi, Cd:

Nitrates and acetates of all. Copper, cadmium and bismuth sulphates, mercuric, copper and cadmium chlorides, silver fluoride, cadmium bromide and iodide, copper chromate, mercuric bromide and cyanide. Bismuth chloride is soluble in little water; more water precipitates BiOCl.

Of the metals of the hydrogen sulphide group:

2d Class: Sn, Sb, As:

Stannous sulphate, chloride and iodide, stannic chloride and iodide, arsenic acid.

2. *Soluble with difficulty in water, easily soluble in* HCl *or* NO_3H.

Of the alkaline earths:

Calcium hydroxide, strontium and calcium chromates, calcium sulphide, magnesium tartrate, borate and oxalate. Calcium sulphate is more easily soluble in HCl than in water.

Of the metals of the H_2S *group:* 1st Class:

Mercuric chromate, silver and mercurous sulphate, bismuth bromide, lead chloride and iodide. Lead chloride is more easily soluble in *hot* water than in HCl.

Of the metals of the H_2S *group:* 2d Class:

Antimonous chloride, bromide and iodide (because an excess of water decomposes them), arsenious acid.

3. *Insoluble in water, soluble in* HCl, NO_3H, *or in aqua regia.*

Of the alkaline earths:

Barium chromate, magnesium oxide, phosphates, borates, oxalates and tartrates of Ba, Sr, Ca; carbonates and silicates of all four.

Of the earths, the oxides, phosphates and borates of Al and Cr, aluminium oxalate.

Of the metals of the $(NH_4)_2S$ *group:*

The oxides, phosphates, carbonates, and sulphides.

Of the metals of the H_2S *group:* 1st Class:

The oxides, phosphates, sulphides, carbonates of all, mercurous chloride, bromide, and iodide, mercuric iodide, bismuth iodide, silver arseniate, silver and copper arsenites, silver, mercurous and bismuth chromates.

Of the metals of the H_2S *group:* 2d Class:

Stannous oxide, antimony oxide, antimony sulphate, stannic phosphate (insoluble in H_2O and NO_3H), and the sulphides.

4. *Insoluble in water, difficultly soluble in acids.*

Of the alkaline earths: the fluorides.

Of the metals of the H_2S *group:* lead sulphate and chromate.

5. *Insoluble in water and in acids.*

Of the alkaline earths: barium and strontium sulphates.

Of the metals of the H_2S *group:* the halogen salts of silver (excepting the fluoride), silver cyanide.

Further, many silicates and oxides. See under X.

IV.—SEPARATION OF THE BASES INTO GROUPS.

These are precipitated by:

I.	II.	III.	IV.	V.
HCl in acid or neutral solution.	H_2S in solutions acidulated with HCl or NO_3H.	$(NH_4)_2S+NH_3$.	$CO_3(NH_4)_2$ in presence of NH_3 and NH_4Cl.	$PO_4Na_2H+NH_3+NH_4Cl$.
Ag_2O	Ag_2O	Al_2O_3	Ba	Mg
Hg_2O	Hg_2O	Cr_2O_3	Sr	
PbO partly	HgO	NiO†	Ca	
	PbO	CoO†		
	CuO	FeO		
	CdO	Fe_2O_3		
	BiO	ZnO		
	Sb_2O_3	MnO		
	Sb_2O_5			
	As_2O_3			
	As_2O_5 *			
	SnO			
	SnO_2			

Ammonia and *ammonium sulphide* precipitate further $AlPO_4$, and the phosphates and oxalates of the alkaline earths; if, therefore, the tests for acids show the presence of PO_4H_3 or $C_2O_4H_2$, these must be removed before testing for the bases.

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* If the precipitate No. II is treated with $(NH_4)_2S$ (if Cu be present, with K_2S), the sulphides corresponding to these six oxides dissolve.

† If the precipitate No. III is treated with cold dilute HCl, the sulphides of Co and Ni remain undissolved.

V.—Detection of Bases.

1. *Treatment of the precipitates formed by* HCl *and by* H_2S. After making preliminary tests, and tests of solubility, proceed as follows:

If the solvent used was water or nitric acid, add a little hydrochloric acid; if a white precipitate is formed, which is not dissolved by boiling with water, filter; the precipitate is either AgCl, HgCl, or a mixture of both; treat it with warm aqua regia. If it dissolves it was HgCl, which was oxidized by aqua regia to $HgCl_2$. Prove the presence of $HgCl_2$ by heating with $SnCl_2$. This reagent precipitates HgCl and Hg (give equation).

The part insoluble in aqua regia is AgCl, easily soluble in NH_3 (?), or if AgCl is treated with zinc and dilute sulphuric acid, metallic silver is formed (?).

The solution after removing the precipitate formed by HCl may be treated at once with H_2S, if it does not contain nitric acid or aqua regia; if much of these acids be present, evaporate the solution nearly to dryness to drive off the excess of acid, and dissolve the residue in water or very dilute HCl; if but little NO_3H or aqua regia is present, dilute with warm water; (why are these precautions necessary?). Now conduct a weak current of H_2S into the warm solution, until the solution, when shaken and exposed to the air, still retains the strong odor of H_2S. If a precipitate is formed it may consist of one or more of the following sulphides:

Colors of the Sulphides.

Black.	Yellow.	Orange.	Brown.
PbS	CdS	Sb_2S_3	SnS
CuS	SnS_2	Sb_2S_5	Bi_2S_3
Ag_2S	As_2S_3		
Hg_2S	As_2S_5		
HgS			

We divide these sulphides into two classes:

A. *The group soluble in* $(NH_4)_2S$ contains the sulphides of As, Sb, Sn.

Treat a part of the H_2S precipitate with $(NH_4)_2S$.

The sulphides of these metals dissolve, forming sulpho salts, according to the equations:

$SnS + (NH_4)_2S + S = SnS_3(NH_4)_2$.

$As_2S_3 + 3(NH_4)_2S + S_2 = 2[AsS_4(NH_4)_3]$.

$Sb_2S_3 + 3(NH_4)_2S + S_2 = 2[SbS_4(NH_4)_3]$.

$SnS_2 + (NH_4)_2S = SnS_3(NH_4)_2$.

$As_2S_5 + 3(NH_4)_2S = 2[AsS_4(NH_4)_3]$.

$Sb_2S_5 + 3(NH_4)_2S = 2[SbS_4(NH_4)_3]$.

If the substance examined contains copper, which may be recognized by the color of the solution (blue), or by the preliminary tests, treat the H_2S precipitate with K_2S, because CuS is somewhat soluble in $(NH_4)_2S$. Prepare K_2S by dividing a solution of KOH into two equal parts; saturate one part with H_2S, then add the other. (Give equations.)

Always use yellow polysulphide of NH_4 or K. Why?

Add dilute SO_4H_2 to the $(NH_4)_2S_2$ with which you have treated the metal sulphides. If only white milky sulphur is precipitated [decomposition of ammonium polysulphide by H_2SO_4 (?)], none of the H_2S precipi-

tate was dissolved; (in this case treat as directed under B); but if you notice a flaky colored precipitate, sulphides of Sn, Sb, or As are present.

The precipitate caused by SO_4H_2 may contain SnS_2, As_2S_5, Sb_2S_5. (Give equations.)

Heat the precipitate gently with a concentrated solution of ammonium carbonate, and filter from the part which remains undissolved. As_2S_5 is dissolved:

$$4As_2S_5 + 12CO_3(NH_4)_2 = 5AsS_4(NH_4)_3 + 3AsO_4(NH_4)_3 + 12CO_2.$$

Add to this solution HCl in excess, and ClO_3K; heat until all Cl is driven off; you now have arsenic acid in solution (?); prove its presence either by adding an excess of NH_3 and mixing with NH_4Cl and SO_4Mg (what would the precipitate be?), or by testing the solution (after driving off Cl) in Marsh's apparatus.

The residue insoluble in $(NH_4)_2CO_3$ may be SnS_2 and Sb_2S_5; dissolve in HCl, adding $KClO_3$; drive off the Cl, dilute the solution with water, bring it into a platinum dish and add a little granulated zinc (instead of the platinum dish, a small porcelain dish in which a piece of platinum foil is laid may be used); metallic antimony separates in the form of a black coating on the platinum, and metallic tin as a spongy mass; dissolve the spongy tin with the rest of the zinc in HCl, and add a solution of $HgCl_2$. The presence of the smallest trace of tin causes a precipitation of HgCl, and if tin enough is present, black Hg is precipitated.

Treat the coating of Sb on the platinum with NO_3H; the coating turns white; touch the white coating with a glass rod moistened with a solution of silver nitrate in ammonia, and black spots are formed:

$$Sb_2O_3 + 4Ag_2O = Sb_2O_5 + 2Ag_4O.$$

Another method of separating Sn and Sb is to evaporate the sulphides with nitric acid to dryness, which changes them to metastannic acid, SnO_3H_2, and metantimonic acid, SbO_3H; fuse this residue with an excess of sodium hydroxide in a silver (or Hessian) crucible; sodium stannate and sodium pyroantimoniate are formed; sodium stannate is easily soluble in water, and may be precipitated from the aqueous solution —after acidulating with HCl—as sulphide. Sodium pyroantimoniate, $Sb_2O_7Na_2H_2$, is but slightly soluble in water; dissolve it in HCl to which you have added tartaric acid [to prevent the precipitation of basic salt (?)], and precipitate with H_2S.

B. *The group insoluble in* $(NH_4)_2S$ contains the sulphides of Pb, Ag, Cu, Bi, Cd, and Hg.

Treat the precipitate with warm concentrated nitric acid; an undissolved residue may contain HgS, or $PbSO_4$ (formed by oxidation of PbS), or sulphur, which is frequently colored by minute particles of sulphides. Treat this residue with basic ammonium tartrate; this dissolves the lead sulphate (which can be reprecipitated from the solution by acidulating it); heat the residue with aqua regia, evaporate the excess of acid, and test for mercury with $SnCl_2$. A residue of sulphur burns with blue flame when heated on the platinum foil, forming SO_2.

To the portion soluble in NO_3H add dilute SO_4H_2,

and evaporate until heavy white fumes of SO_4H_2 are given off; now dilute with water; a white turbidity or precipitate is SO_4Pb, soluble in basic ammonium tartrate.

Add HCl to the filtrate from SO_4Pb; a white precipitate is AgCl; filter, and add an excess of NH_3 to the filtrate. If Bi is present it is precipitated as white BiOOH. Filter, dissolve the residue in HCl, make the solution alkaline, and add alkaline $SnCl_2$ solution; black bismuth suboxide (BiO) is precipitated (?).

If when ammonia was added to precipitate the bismuth the solution turned blue, the presence of Cu is shown; add to the filtrate from BiOOH, potassium cyanide until the blue color disappears; the colorless solution now contains the Cu as a double salt of cuprous cyanide and potassium cyanide, $Cu_2(CN)_26KCN$, and cadmium as $Cd(CN)_22KCN$. Conduct H_2S into the solution; if a yellow precipitate is formed it is CdS; the cuprous salt is not decomposed by H_2S. Filter the CdS, fuse it with soda on charcoal, and note reaction. The copper can be isolated in the filtrate from CdS by adding SO_4H_2 till all HCN is driven off, and from the solution which now contains copper sulphate, the Cu is precipitated by potassium ferrocyanide as reddish brown copper ferrocyanide.

Note.—When H_2S is conducted into the solution of a substance, sulphur is sometimes precipitated, because the H_2S acts as reducing agent toward the higher oxygen compounds of the metals of the $(NH_4)_2S$ group:

$$Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S;$$

$$Cr_2O_7K_2 + 8HCl + 3H_2S = Cr_2Cl_6 + 2KCl + 7H_2O + 3S.$$

VI.—DETECTION OF BASES.

2. *Treatment of the precipitate formed by* NH_3 *and* $(NH_4)_2S$.

Add to the solution of the substance (after filtering from the precipitate formed by H_2S) ammonia, ammonium chloride, and ammonium sulphide. The precipitate may contain Al and Cr as hydroxides, Fe, Mn, Co, Ni, Zn as sulphides.

Color of these Compounds.

White.	Green.	Black.	Flesh Color.
$Al(OH)_3$	$Cr(OH)_3$	FeS	MnS
ZnS		NiS	
		CoS	

Besides the above, if phosphoric or oxalic acid is present, the following compounds may be precipitated by $(NH_4)_2S$:

PO_4MgNH_4, PO_4Al, and the oxalates and phosphates of Ca, Ba, and Sr.

It is better, therefore, before adding $(NH_4)_2S$ to the solution, to test for PO_4H_3 and $C_2O_4H_2$. Test for PO_4H_3 by adding ammonium molybdate to the solution of the substance in NO_3H. If no As is present, the yellow precipitate formed by warming the mixture gently is proof of the presence of PO_4H_3 (?); but AsO_4H_3 yields a similar precipitate with ammonium molybdate; how can you prove the presence of PO_4H_3 when AsO_4H_3 is contained in the substance examined?

Heat the dry substance with conc. SO_4H_2. If both CO and CO_2 are given off, $C_2O_4H_2$ is present.

Treat with Sn and NO_3H; for details see the chapter on Sodium Phosphate.

If $C_2O_4H_2$ is present, evaporate the solution to dryness, and heat the residue in a platinum dish over the blast flame. The oxalic acid is destroyed; carbonates or oxides of the metals remain; dissolve the residue in NO_3H, and precipitate with NH_3, NH_4Cl, and $(NH_4)_2S$.

Further Treatment of the $(NH_4)_2S$ *Precipitate.*

Pour cold very dilute HCl over the precipitate; this dissolves all compounds excepting CoS and NiS, which are but little soluble in $(NH_4)_2S$ and remain for the most part on the filter.

A. *Treatment of the portion of the precipitate insoluble in* HCl.

Dissolve the CoS and NiS in aqua regia, evaporate to dryness, dissolve the residue in water acidulated with HCl, and add KCN until the precipitate of $Co(CN)_2$ and $Ni(CN)_2$ first formed is entirely redissolved, forming nickel-potassium cyanide, $Ni(CN)_2$ 2KCN, a double salt, and potassium cobalto-cyanide, $Co(CN)_6K_4$, a salt analogous in composition to $Fe(CN)_6K_4$. Now add *one* or *two* drops of the HCl to the solution, and heat it nearly to the boiling point, then allow it to stand five minutes. The $Co(CN)_6K_4$ is oxidized by the oxygen of the air, according to the equation:

$$2Co(CN)_6K_4 + O + H_2O = Co_2(CN)_{12}K_6 + 2KOH.$$

This compound, potassium cobalti-cyanide, the potassium salt of cobalti-hydrocyanic acid, is very stable, and is not decomposed by dilute acids nor by oxidizing agents.

Nickel forms no such compound, but is still in solution as $Ni(CN)_2\,2KCN$. If dilute HCl in excess is now added, $Ni(CN)_2$ is precipitated:

$$Ni(CN)_2\,2KCN + 2HCl = Ni(CN)_2 + 2KCl + 2HCN.$$

Still more characteristic is the action of oxidizing agents. Add to the solution containing $CO_2(CN)_{12}K_6$ and $Ni(CN)_2\,2KCN$, sodium hydroxide in large excess. Warm gently and add bromine water. The nickel is precipitated as black $Ni(OH)_3$, nickelic hydroxide:

$$Ni(CN)_2\,2KCN + 9Br + 3KOH = Ni(OH)_3 + 5KBr + 4(BrCN).$$

The $Co_2(CN)_{12}K_6$ remains unchanged in solution; add NO_3H to the solution, evaporate it to dryness, and ignite. The cobalt is present in the residue in the form of CoO; wash the residue with water to remove KOH, and test for Co by means of the microcosmic bead.

B. *Treatment of the portion of the* $(NH_4)_2S$ *precipitate which is soluble in* HCl.

Boil the solution with nitric acid to oxidize ferrous to ferric salt; [test the completeness of the oxidation by adding potassium ferricyanide to a sample of the solution (?)]; add sodium carbonate to the solution until precipitation just commences; dissolve this precipitate in a drop of HCl. We now have a solution nearly neutral; add sodium acetate and *two* or *three drops* of acetic acid; dilute with much water, and heat to boiling. As soon as the solution boils, remove the lamp; the precipitate may contain the hydroxides or basic acetates

of Al, Cr, Fe. Allow it to settle, and filter the hot solution (why hot?). If the operation was successful the filtrate must be colorless, and may contain the acetates of Zn and Mn, and (if Co and Ni were present) the acetates of Co and Ni.

Conduct H_2S into the boiling solution: white ZnS is precipitated. Filter; the filtrate contains manganese. If traces of Co and Ni are present, the precipitate will be gray or black. If it is white, heat it with cobalt solution on the platinum wire (?); if black, dissolve it in NO_3H, add excess of NH_3, then excess of tartaric acid, and conduct H_2S into the solution. White ZnS is precipitated; cobalt and nickel tartrates remain in solution.

The zinc may also be separated from traces of Co and Ni by the following method: Dissolve the sulphide in NO_3H, and add an excess of NaOH; Ni and Co remain precipitated as hydroxides; Zn dissolves as sodium zincate, $Zn(ONa)_2$; filter, and conduct H_2S into the solution; white ZnS is precipitated.

Add NaOH to the filtrate containing Mn until *most* of the free acetic acid is neutralized; heat gently and add bromine water. Allow the liquid to stand for an hour. All Mn is slowly precipitated as MnO_4H_4 of dark brown color. At the same time test for manganese in the original substance by fusion on platinum foil with Na_2CO_3 and KNO_3, or with NO_3H and minium (?).

Dissolve the precipitate containing Fe, Al, Cr in a little HCl, add an excess of cold NaOH. Fe is precipitated (?). Al and Cr are first precipitated, then redissolved (?).. Filter; dissolve the precipitate in HCl, and note its action with $Fe(CN)_6K_4$.

The *quickest* way to separate Al and Cr is to heat the alkaline solution (which, if Cr is present, is green) to boiling; Cr is precipitated, Al remains in solution (?). A better and more exact way is to add to the alkaline solution bromine water, and heat until the solution loses its green color and turns yellow.

$Br_2 + 2NaOH = NaBr + NaOBr + H_2O$;
$2Cr(ONa)_3 + 3NaOBr + H_2O =$
$2CrO_4Na_2 + 3NaBr + 2NaOH$.

Add to the solution NH_4Cl in excess and boil; all Al is precipitated as $Al(OH)_3$; at the same time NH_3 and N escape:

$Al(ONa)_3 + 3NH_4Cl = Al(OH)_3 + 3NaCl + 3NH_3$;
$3BrONa + 2NH_3 = 3NaBr + 3H_2O + N_2$.

Filter the $Al(OH)_3$ and test on charcoal with cobalt solution.

The filtrate contains the Cr as chromate; treat it with reducing agents, such at SO_2, or HCl and alcohol. It will be again reduced to chromium salt, which you may precipitate by continued boiling with NH_3, as $Cr(OH)_3$, which colors the borax bead green.

3. *Treatment of the precipitate formed by ammonium carbonate.*

Add to the filtrate from the $(NH_4)_2S$ precipitate, $(NH_4)_2CO_3$. [If the solution examined does not already contain NH_4Cl and NH_3, add these reagents before adding $(NH_4)_2CO_3$.] This reagent precipitates all Ba, Sr, Ca as carbonates, if the solution is heated to the boiling point. Why is the presence of NH_4Cl necessary?

Filter the precipitate; wash with water.

The two best methods of separation of Ca, Sr, and Ba are given in full at the close of the chapter on Calcium Chloride. The student should use both these methods until quite familiar with them; but, as they require much time, a quicker way of detecting Ba, Sr, and Ca is desirable, and in most cases the following will suffice:

Retain a little of the washed precipitated carbonate for flame reactions, and dissolve the remainder in HCl; divide the solution into three parts.

I. Add to one part SO_4Ca solution; a precipitate formed at once or after standing a few moments is SO_4Ba or SO_4Sr. If no precipitate is formed, the substance examined contains only Ca.

II. If a precipitate was formed, add to the second part of the HCl solution, SO_4Sr; a precipitate is SO_4Ba.

III. If Ba or Sr was found, test for Ca as follows: dilute the third portion of the HCl solution with water, add dilute SO_4H_2, and filter from the precipitated sulphates of Ba and Sr; add to the filtrate NH_3 and $C_2O_4(NH_4)_2$; a precipitate is C_2O_4Ca.

IV. If Ba was found, the presence of Sr can be proved by the flame test; bring on the platinum wire a little of the precipitated carbonate, heat gently in the flame, moisten with HCl, and put it slowly in the flame. $SrCl_2$ will flash up with a dark red flame while the wire is still distant ¼ inch from the flame of the burner; $CaCl_2$ does *not* impart color to the flame unless exposed to a higher temperature than is necessary for $SrCl_2$.

4. *Test for magnesia.*

Add to a *small portion* of the filtrate from the alkaline earth carbonates, NH_4Cl, NH_3, and PO_4Na_2H. A white crystalline precipitate is $MgNH_4PO_4 + 6H_2O$.

If it is not necessary to test for alkalies the above suffices. If it is desired to test for NaOH or KOH, PO_4Na_2H should not, of course, be used as reagent. Ammonium phosphate may be used, but as the residue of PO_4H_3 cannot easily be removed, it is better to proceed as follows:

Evaporate the solution containing Mg to dryness, and drive off ammonium salts; dissolve the residue in water, and add an excess of $Ba(OH)_2$; magnesium hydroxide is precipitated. Filter; remove the excess of $Ba(OH)_2$ from the filtrate with $(NH_4)_2CO_3$, evaporate the filtrate to dryness to drive off ammonium salts. The residue is Na or K salt. Test the precipitated $Mg(OH)_2$ with cobalt solution on charcoal.

5. *Test for alkalies.*

After removing all other bases, make a flame test for K and Na with some of the residue. Dissolve the remainder in water and divide into three parts.

Test in the first part for K with $C_4H_6O_6$.

In the second, test for Na with potassium pyroantimoniate, which forms with Na compounds a precipitate of sodium pyroantimoniate, $Sb_2O_7H_2Na_2$.

Add to a few drops of the third part a drop of HCl and an excess of $PtCl_4$; evaporate to dryness on the water-bath, and treat the residue with 90 per cent alcohol, in which $PtCl_6K_2$ is insoluble, but $PtCl_6Na_2$ easily soluble; by evaporating the alcohol from the filtrate the $PtCl_6Na_2$ is isolated.

Test the original substance examined for NH_3 by boiling with NaOH, or more accurately, by testing with $Ca(OH)_2$.

X.—Decomposition of Substances insoluble in Water and Acids.

To this class belong lead, strontium and barium sulphates, some fluorides, silicic acid, many silicates, stannic anhydride, antimonic acid, aluminium oxide, chromium oxide, etc.

It is necessary to change these substances into compounds soluble in water or acids.

Lead sulphate is soluble in basic ammonium tartrate. The other substances mentioned must be fused with proper reagents; silicic acid and silicates are either fused, or decomposed with HFl.

The reagents used in fusions are alkaline carbonates, monopotassium sulphate, sodium hydroxide, a mixture of sodium carbonate with potassium nitrate, and a mixture of sodium carbonate with sulphur.

Necessary Precautions.—Make a careful preliminary test of the substance before fusion; no substance containing lead, tin, bismuth, or antimony, no easily reducible oxides, no free alkali, or sulphides, should be fused in a platinum crucible. Fusions with KNO_3 should be made in an iron or nickel crucible. In fusing in the platinum crucible with alkaline carbonates, the substance should be finely powdered and thoroughly mixed with the carbonates. The crucible should not be more than one-third full, and should be heated five to ten minutes over the blast lamp till the mixture is thoroughly fused and bubbling has ceased.

The flame must be clear and non-luminous; the crucible must be heated on a pipe stem or platinum triangle, not on iron.

If after fusion the cooled mass adheres to the crucible, lay the crucible on its side in a porcelain dish, add distilled water, and boil till the mass is loosened.

If the crucible is not clean, dip your moistened finger in fine sand and rub the platinum gently; if this does not suffice, fuse some monopotassium sulphate in the crucible, and dissolve the residue in water.

Fusions with NaOH must be made in a silver crucible; porcelain or platinum crucibles must not be used; heat with the ordinary Bunsen burner.

Fusions with SO_4KH may be made in a platinum crucible; heat with a Bunsen burner; heat so that fumes of SO_3 slowly escape.

If the preliminary test yields a sulphide without metal bead, the substance contains SO_4Ba or SO_4Sr; mix the substance with four times its weight of a mixture of equal parts of Na_2CO_3 and K_2CO_3, and fuse in a platinum crucible; powder the fused mass; boil with water, filter and wash; the residue is $BaCO_3$ or $SrCO_3$, which treat as already described.

If the preliminary test yields a sulphide and metal bead with yellow coating, treat with basic ammonium tartrate; a residue of $BaSO_4$ or $SrSO_4$ should be fused.

If the preliminary test shows SiO_2 you may have silicic acid or a silicate; *pure amorphous silicic acid* is soluble in a solution of Na_2CO_3; *crystallized* SiO_2 must be fused in a platinum crucible with alkali carbonate.

Reduce in an agate mortar to an impalpable powder; evaporate a part of the substance with HCl repeatedly to dryness; if the residue can be rubbed with a glass stirring-rod without grating on the dish, the silicate is *decomposable by* HCl; in this case treat the residue with water acidulated with HCl, and filter; the residue is silicic acid; the base should be sought in the filtrate.

If the silicate *is not decomposed by* HCl, fuse with alkaline carbonate in a platinum crucible, treat the fused mass with HCl, evaporating to dryness, etc., etc.

To test for K *and* Na in such silicate, evaporate with HFl and SO_4H_2 repeatedly to dryness in a platinum dish; silicon escapes as $SiFl_4$; the bases are in the residue as sulphates.

Insoluble fluorides should be fused with alkaline carbonate; powder the fused mass, boil with water, and filter; alkali fluoride is in the filtrate; the residue contains the bases which were combined with the HFl.

Insoluble aluminium oxide is best fused in a platinum crucible with SO_4KH. A mixture of Al_2O_3 and Cr_2O_3 as well as some insoluble chromites are best fused with a mixture of Na_2CO_3 and KNO_3 in an iron or nickel crucible, the Cr is oxidized to chromate, the Al is in the fused mass as aluminate.

If the preliminary test shows the presence of Sn or Sb, treat the insoluble substance with warm NO_3H, evaporate the acid, fuse the residue (which must not contain lead) with an excess of NaOH in a silver crucible. Tin is changed to sodium stannate, soluble in water; antimony to sodium pyroantimoniate, which is almost insoluble in water.

XI.—PRELIMINARY TESTS FOR ACIDS.

Put a little of the dry substance into a test tube, pour upon it three or four times its volume of conc. SO_4H_2, and heat gently. You will notice,

No escape of gas in presence of the salts of	Escape of colored gas in presence of the salts of	Escape of colorless gas in presence of the salts of
Iodic Acid	Hydriodic Acid	Hydrochloric Acid
Sulphuric Acid	Hydrobromic Acid	Hydrofluoric Acid
Silicic Acid	Hypochlorous Acid	Nitric Acid
Boric Acid	Chloric Acid	Hydrocyanic Acid
Phosphoric Acid	Nitrous Acid	Carbonic Acid
Arsenic Acid		Sulphurous Acid
Arsenious Acid		Hyposulphurous Acid
		Chromic Acid
		Oxalic Acid
		Tartaric Acid
		Citric Acid
		Hydrogen Sulphide

XII.—PRINCIPAL REACTIONS OF THE MORE COMMON ACIDS.

Soluble *chlorides* treated with H_2SO_4 give off HCl as colorless fumes of penetrating odor, which form a white precipitate with NO_3Ag.

Soluble *bromides* treated with conc. SO_4H_2 give off a brown gas (?); this vapor colors starch paste yellow. Soluble bromides precipitate NO_3Ag (?). Chlorine water sets Br free from bromide solutions; use CS_2 to detect traces of Br.

Iodides when treated with conc. SO_4H_2 yield violet vapors of iodine, which give characteristic reaction with

starch paste. Soluble iodides precipitate NO_3Ag. Chlorine or bromine water added to the solution of an iodide sets iodine free, soluble with violet color in CS_2. An excess of Cl or Br water causes the iodine to disappear (?).

Treated in a test tube with conc. SO_4H_2, fluorides give colorless fumes which form a white coating on a drop of distilled water on a glass rod. $CaCl_2$ precipitates soluble fluorides, forming gelatinous $CaFl_2$, insoluble in acetic acid. NO_3Ag does not form a precipitate with fluorides.

Chlorates with conc. SO_4H_2 yield explosive yellow fumes of Cl_2O_4. Free ClO_3H bleaches indigo solution; chlorates in neutral or alkaline solution do not bleach organic colors. Chlorates heated with the blowpipe on charcoal cause explosive combustion of the charcoal.

Hypochlorites give Cl when treated with conc. SO_4H_2, and bleach indigo solution in neutral or alkaline solution.

Iodates treated with conc. SO_4H_2 give no iodine unless a reducing agent (for example $FeSO_4$) is present. Iodates heated on charcoal cause explosive combustion. In presence of iodides, the iodates treated with acetic acid yield I:

$$IO_3H + 5HI = 3H_2O + 6I.$$

Nitrates yield with conc. SO_4H_2 fumes of NO_3H which are nearly colorless; if Cu or SO_4Fe is added, red vapors are evolved. The minutest traces of nitrates yield with SO_4Fe and conc. SO_4H_2 a brown ring.

Nitrites yield with dilute SO_4H_2 red vapors. Nitrous acid added to an iodide sets I free, which may be detected with starch paste.

Acetates warmed with conc. SO_4H_2 and alcohol yield acetic ether, which can be recognized by its agreeable odor. Neutral acetates color $FeCl_3$ solution dark red.

Cyanides treated with conc. SO_4H_2 give off CO; treated with dilute SO_4H_2, cyanides give off HCN. Soluble cyanides precipitate from $AgNO_3$ white silver cyanide (soluble in NH_3, $Na_2S_2O_3$, and KCN), which is decomposed by conc. SO_4H_2. Only the cyanides of the alkalies, alkaline earths, and mercuric cyanide, and most double cyanides are soluble in water. To test for soluble cyanides, add to the solution a ferrous salt containing ferric salt (use partially oxidized $FeSO_4$), then add NaOH in excess, and boil for a few moments; now add HCl to dissolve the precipitated $Fe(OH)_3$; an undissolved residue of Prussian blue proves the presence of CN in the substance examined (?). Another test is to add to the solution of the substance to be examined a few drops of NH_3 and yellow ammonium sulphide, evaporate on the water-bath to dryness, and dissolve the residue in water. If cyanides were present, ammonium sulphocyanide is formed, which colors ferric chloride solution red (?).

Acids set CO_2 free from *carbonates*; CO_2 conducted into baryta water or lime water precipitates white carbonate, soluble in acids.

Silicates and SiO_2 do not react with conc. SO_4H_2. They form a skeleton in the microcosmic bead; only the alkali silicates are soluble in water. Silicic acid and many silicates, when moistened with $Co(NO_3)_2$

and heated on the charcoal, yield a blue mass. Concentrated solutions of soluble silicates yield when NO_3H or HCl is added, gelatinous $Si(OH)_4$.

Sulphates treated with SO_4H_2 form primary sulphates; reduced on charcoal, sulphates yield a hepar; sulphates soluble in HCl form with $BaCl_2$ white insoluble $BaSO_4$; [avoid concentrated solutions in this last reaction (?)].

Sulphites treated with conc. SO_4H_2 yield a mixture of H_2S and SO_2 (?); dilute SO_4H_2 gives SO_2. Sulphites precipitate from NO_3Ag metallic silver, $2NO_3Ag + SO_3Na_2 + H_2O = 2NO_3Na + Ag_2 + SO_4H_2$; reduced on charcoal with soda, the sulphites yield a hepar. When the sulphites are heated alone, a mixture of sulphate and sulphide is formed (?). SO_2 bleaches iodine solution (?).

From *hyposulphites* conc. SO_4H_2 causes the evolution of a mixture of SO_2 and H_2S, at the same time precipitating S. Dilute acids give SO_2 and precipitate S. Hyposulphites precipitate from NO_3Ag, Ag_2S.

$$S_2O_3Na_2 + 2NO_3Ag + H_2O = 2NO_3Na + Ag_2S + SO_4H_2.$$

Examine the filtrate for SO_4H_2.

Reduced with soda on charcoal, the hyposulphites form hepar. Fused alone, they yield a mixture of sulphate and polysulphide. They bleach iodine solution:

$$2S_2O_3Na_2 + 2I = 2INa + S_4O_6Na_2,$$

sodium tetrathionate being formed.

Sulphides which are decomposed by SO_4H_2 or HCl give H_2S when treated with these acids. When conc. H_2SO_4 is used, the H_2S is partially decomposed, precipitating S (?). Test for escaping H_2S with a strip of paper moistened with lead acetate; H_2S turns it black (?). Insoluble sulphides are decomposed by NO_3H or aqua regia, separating S, which may be partially or quite oxidized to SO_4H_2. The sulphides soluble in water (alkali sulphides) yield (when diluted with much water) a violet color with a solution of sodium nitroprussiate.

Chromates treated with conc. SO_4H_2 give oxygen (?); treated with conc. HCl they evolve chlorine (?); they color the microcosmic bead green, in consequence of their reduction to chromium oxide. Aqueous acidified solutions of chromates are reduced to chromium oxide salts by H_2S, by SO_3H_2, and by dilute HCl and alcohol (?). From these solutions ammonia precipitates green chromium hydroxide; $(NH_4)_2S$ also reduces chromates. NO_3Ag precipitates from *neutral* solutions of chromates reddish brown silver chromate.

Oxalic acid or *oxalates* treated with conc. SO_4H_2 evolve CO_2 and CO, leaving a little carbon; conduct the escaping gas through lime water, which absorbs the CO_2, and ignite the CO, which burns with blue flame. Calcium oxalate is insoluble in acetic acid, soluble after ignition, giving off CO_2.

Tartaric acid and *tartrates* treated with conc. SO_4H_2 evolve SO_2, CO_2, CO, and leave a residue of carbon; ignited on platinum foil, the odor of burned sugar is noticeable. The primary potassium salt

(cream of tartar) is soluble with difficulty in cold water. The secondary alkali salts are easily soluble in cold water. The calcium salt is insoluble in water, soluble in acetic acid, NH_4Cl, or KOH (difference from calcium oxalate); the solution in KOH becomes turbid when boiled.

Phosphoric acid and *phosphates* suffer no change when treated with conc. SO_4H_2. The neutral solution of phosphates treated with a mixture of NH_3, NH_4Cl, and $MgSO_4$, yields a crystalline precipitate of ammonium magnesium phosphate. The phosphates of the alkaline earths are soluble in acetic acid. Ferric phosphate and aluminium phosphate are insoluble in acetic acid. If the solution of a phosphate in nitric acid is warmed gently with ammonium molybdate, a yellow precipitate of ammonium phospho-molybdate is formed. NO_3Ag precipitates from solutions of phosphates yellow Ag_3PO_4, soluble in NH_3 and in NO_3H. $FeCl_3$ precipitates $FePO_4$. Pyro- and meta-phosphates form white precipitates with NO_3Ag.

Arseniates do not react with conc. SO_4H_2; fused with soda on charcoal, the characteristic odor is noticeable. With magnesia mixture, with ammonium molybdate, and with NO_3Ag, arseniates react exactly like phosphates, excepting that AsO_4Ag_3 is brownish red and soluble in NH_4NO_3.

The behavior of arseniates toward H_2S (particularly after reduction with SO_3H_2) makes it easy to distinguish and separate them from phosphates.

Arsenic trioxide (*arsenious acid*) and *arsenites* behave like arseniates with conc. SO_4H_2, H_2S, and on charcoal, but yield no difficultly soluble precipitate with magnesia mixture. Arsenites do not react with ammonium molybdate. Silver arsenite is yellow; on boiling the solution of silver arsenite in NH_3, a black precipitate of metallic silver is formed, arsenious acid being oxidized to arsenic acid.

Boracic acid does not react with conc. SO_4H_2; it colors the alcohol flame green; this reaction occurs with borates on adding conc. SO_4H_2 and alcohol and igniting; it depends on the formation of boracic ether; the green color is particularly noticeable on the edges of the flame and toward the close of the reaction. An aqueous solution of boracic acid, or of a borate, acidified with HCl, colors turmeric paper reddish brown; the color cannot be clearly seen till the paper is dried. Conc. HCl or NO_3H precipitates crystalline boracic acid from solutions of borates.

Borates form with silver nitrate a white precipitate of silver borate, but *only* when the solutions are *concentrated;* the precipitate is soluble in NH_3 and in NO_3H.

Ferrocyanides treated with conc. SO_4H_2 evolve CO; treated with dilute SO_4H_2 they evolve HCN. With ferric salts they form Prussian blue.

SEPARATION OF CHLORINE, BROMINE, AND IODINE.

To test a soluble substance for the halogens, pour a little CS_2 into the solution, and add chlorine water cautiously; if iodine is present it is set free, and colors the CS_2 violet. Now add chlorine water till the violet

color of the CS_2 disappears; this depends on the formation and decomposition of iodine pentachloride (?).

A further addition of chlorine water acts on bromides if present, setting free the bromine, which colors CS_2 brown. If iodine were found it may be completely separated as cuprous iodide, CuI, by adding $CuSO_4$ and SO_3H_2 to the solution of the original substance. Filter, remove the $CuSO_4$ in the filtrate with H_2S, evaporate the solution to dryness, and test the residue with Cl water for bromine.

To prove the presence of chlorides, mix the powdered substance with potassium bichromate, add conc. SO_4H_2, and heat gently; an evolution of red vapor shows the presence of Cl; the vapor is chromium acichloride. If bromides or iodides are present, conduct the red gas into a solution of KOH or of NH_3. The presence of Cl in the substance examined is proved if Cr can be found in the distillate:

$$Cr_2O_7K_2 + 4KCl + 3SO_4H_2 = 3(SO_4K_2) + 3H_2O + 2CrO_2Cl_2.$$

$$CrO_2Cl_2 + 4NH_3 + 2H_2O = CrO_4(NH_4)_2 + 2NH_4Cl.$$

Bromides thus treated do not form compounds analogous to chromium acichloride, but yield bromine:

$$6HBr + 2CrO_3 = 3H_2O + Cr_2O_3 + 6Br.$$

If it is necessary to test for Cl, Br, or I in the presence of the heavy metals, precipitate the metals with Na_2CO_3, filter, and test the filtrate for the halogens.

Insoluble halogen compounds should be fused with sodium carbonate and potassium carbonate; treat the residue with water, and test for the halogens in the aqueous solution.